Research paper

A study on the combustion of guanidinium 1,5′–bis–1H–tetrazolate / copper(II) oxide

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Abstract

The combustion behavior of the guanidinium 1,5'−bis−1H−tetrazolate (G15B)/copper(Ⅱ) oxide (CuO) mixture, a possible candidate mixture for a gas generating agent, was examined by evaluating the effects of the mixing ratio of G15B/CuO mixtures, the effects of particle size of G15B and the effects of loading pressure for stoichiometric ratio G15B/ CuO mixture, together with the measurement of temperature profiles of burning pellet samples during linear burning rate tests for the stoichiometric ratio mixture. The linear burning rate reached the maximum when the oxygen balance was negative (between −15 g/100 g mixture and −20 g/100 g mixture (or − 15% and − 20%)). It was also shown that there was no noticeable effect of the particle size of G15B on the linear burning rate of stoichiometric ratio G15B/CuO mixture while there was a noticeable decrease in the linear burning rate with an increase in the loading pressure. The measurements of temperature profiles of stoichiometric ratio mixture indicated that the surface temperature varies significantly at constant atmosphere pressure and that the temperature generally increased with an increase in atmosphere pressure. It is suggested that the periodical build−up and consumption of decomposition products of G15B in the burning surface may have occurred during the combustion of G15B/CuO mixtures.

Keywords : Guanidinium 1,5'−bis−1H−tetrazolate, Copper oxide, Combustion behavior, Linear burning rate, Temperature profile

1. Introduction

There have been researches over the years on the development of non−azide gas generating agents for automobile gas generating agents, including tetrazole compounds (especially 5−amino−1H−tetrazole (5−ATZ)[1)−5)] (Fig. 1)), guanidine nitrate[6),7)], nitroguanidine[6),7)] and azodicarbamide (ADCA)[8)]. Recent study[9)] has indicated a relatively high linear burning rate of stoichiometric ratio guanidinium 1,5'−bis−1H−tetrazolate (G15B (Fig. 2))/CuO mixture among some G15B/metal oxide mixtures. In this study, the combustion behavior of G15B/CuO mixtures was examined.

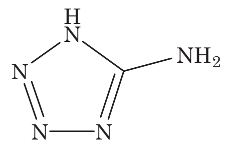

Fig. 1 Chemical structure of 5−amino−tetrazole (5−ATZ)

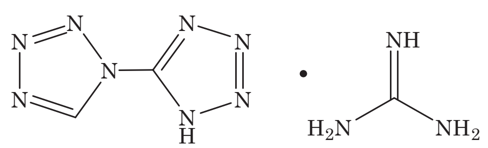

Fig. 2 Chemical structure of guanidinium−1,5'−bis−1H−tetrazolate (G15B)

2. Experimental

2.1 Reagents

G15B was purchased from Toyo Chemicals Co., Ltd. and

Table 1 Mixing ratios of G15B /CuO mixtures

Oxygen balance [g・(100 g mixture)$^{-1}$] (or [%])	−20	−15	−10	−5	0	+5
G15B [wt%]	41.28	36.13	30.99	25.84	20.70	15.55
CuO [wt%]	58.72	63.87	69.01	74.16	79.30	84.45

CuO (purity : 99.9%) was purchased from Kanto Chemicals Co., Ltd. Particle size of G15B was controlled within one of the size ranges, i.e. < 45 μm, 45~75 μm or 75−150 μm, through ball milling and sieving, but CuO was used without ball milling and/or sieving. The powders were dried separately ***in vacuo*** (−76 cm Hg (−1.01 × 10^5 Pa)) in room temperature for at least 24 hours and they were subsequently stored separately in dessicators for at least 24 hours.

2.2 Preparation of the mixtures

G15B and CuO were mixed at one of the mixing ratios given in Table 1, by using a rotary mixer. Each mixture was subsequently dried again ***in vacuo*** (−76 cm Hg (− 1.01 × 10^5 Pa)) in room temperature for at least 24 hours and it was then stored in a desiccator. The dried mixture was used as it is for the sensitivity tests, while the mixture was pelletized as given in the following section for the burning tests.

2.3 Preparation of the pellets for burning tests

2.3.1 Examination of the factors affecting linear burning rate

Four grams of each G15B/CuO mixture was pressed into a cylindrical pellet (diameter 14.8 mm) by a hydraulic press and the surface of the pellet was coated with epoxy resin as a restrictor to ensure cigarette burning of the sample. In order to study the effect of G15B/CuO mixing ratio, G15B with particle size range of 45~75 μm was used and each mixture was pressed at 9.81 MPa. As for the effect of G15B particle size, G15B with either one of the size ranges, i.e. < 45 μm, 45~75 μm and 75 − 150 μm, was used, and the stoichiometric ratio mixture was pressed at a loading pressure of 9.81 MPa for 1 minute. As for the effect of the loading pressure, the stoichiometric ratio mixture was pressed at 5.88, 9.81 or 19.6 MPa, while G15B with a size range of 45~75 μm was used. Before coating the surface of each pellet with epoxy resin, mass and length of the pellet was measured to determine its apparent density, and from the values of true density of G15B measured by Abe et al.[10] as 1.61 g cm^{-3} and that of CuO as 6.315 g cm^{-3} [11], the average void fraction of the pellets for each set of sample mixtures was determined.

2.3.2 Measurement of temperature profiles

One gram of stoichiometric ratio G15B/CuO mixture embedded with a K−type (alumel−chromel) thermocouple (diameter 25 or 50 μm) was pressed to produce a cylindrical pellet for each measurement of temperature profiles. Here also, the surface of the pellet was coated with epoxy resin as a restrictor to ensure end−burning of the sample. With regard to the effect of particle size, G15B with either one of the size range, i.e. < 45 μm, 45~75 μm or 75~150 μm, was used, and the mixture was pressed at 1.96 MPa. As for the effect of loading pressure, G15B with a size range between 45~75 μm, was used, and the mixture was pressed at either 1.47, 1.96 or 2.94 MPa.

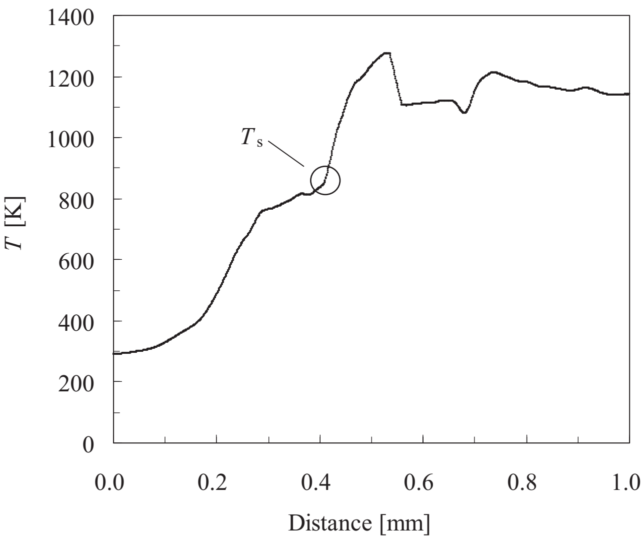

Fig. 3 Typical temperature profile of burning G15B/CuO pellet

2.4 Burning tests

The combustion behavior of G15B/CuO mixtures was examined through linear burning rate test in which the instrumentation and the procedure could be found elsewhere[9]. As for the measurement of temperature profile of a pellet during the linear burning rate test, the data acquired by the K−type thermocouple was recorded on a data recorder (Keyence Co., Ltd., NR−2000) after amplification through a signal conditioner (Kyowa Dengyo Co., Ltd., CDV−230C). During each combustion test of a pellet under a given N_2 pressure (initial gauge pressure) between 0.1~3 MPa, the temperature history inside the pellet was measured. From the temperature profile (a typical example is shown in Fig. 3), the burning surface temperature (T_s) of a pellet was determined following the method of Sabaddel et al. [12].

3. Results and discussion

3.1 Linear burning rate tests

3.1.1 Effect of oxygen balance

The results of the linear burning rate test for G15B/CuO mixtures showing the effect of oxygen balance are given in Fig. 4 and Table 2. Among G15B/CuO mixtures that were examined in this study, the linear burning rates at negative oxygen balance were generally faster than that of stoichiometric ratio mixture. It is estimated that the mixture achieved maximum burning rate at an oxy-

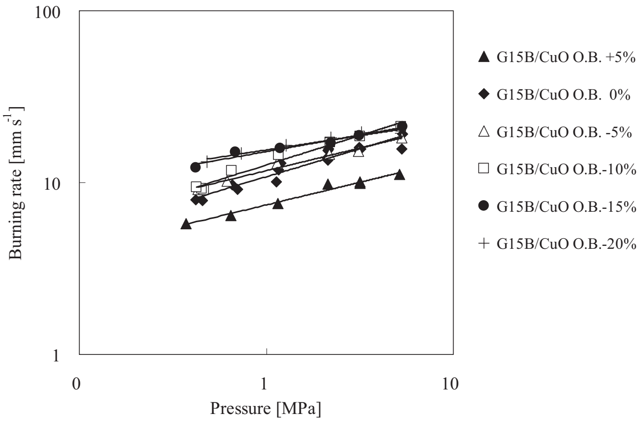

Fig. 4 Effect of oxygen balance on the linear burning rates of G15B/CuO mixtures
("O.B." is the oxygen balance (unit is equivalent to g/(100 g mixture))

Table 2 Effect of G15B particle size on average apparent density of G15B/CuO mixtures

Particle size of G15B [μm]	~45	45~75	75~150
Apparent density [g/cm³]	2.65	2.63	2.65
Void fraction [%]	50.4	50.8	50.4

* Loading pressure 9.81 MPa

gen balance between −15 g/(100 g mixture) ~ −20 g/(100 g mixture) (or −15% ~ −20%). This suggests that what was considered to be a stoichiometric ratio mixture is in fact fuel deficient, suggesting that not all fuel component may be consumed for combustion.

3.1.2 Effect of G15B particle size

Table 3 gives the results of average apparent densities and void fractions of the pellets used for examining the effect of G15B particle size for stoichiometric ratio mixture.

Table 3 Effect of loading pressure on average apparent density of G15B/CuO mixtures

Loading pressure [MPa]	5.88	9.81	19.6
Apparent density [g/cm³]	2.40	2.63	2.91
Void fraction [%]	55.1	50.8	45.5

* Particle size of G15B 45~75 μm

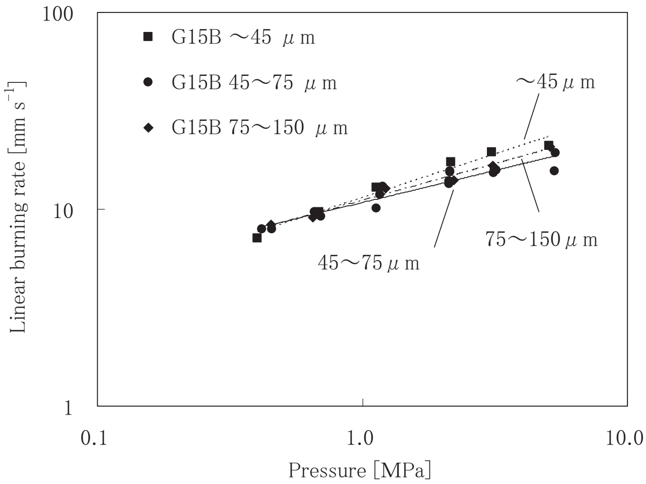

Fig. 5 Effect of particle size on the linear burning rates of G15B/CuO mixtures

Average apparent densities and void fractions were almost equal regardless of the G15B particle size. Figure 5 gives the results of the effect of G15B particle size on the linear burning rate. There was no noticeable effect of the particle size of G15B on the linear burning rate.

3.1.3 Effect of loading pressure

Table 4 gives the average apparent densities and void fractions of the pellets used for examining the effect of the loading pressure. There was an increase in average apparent density and a decrease in void fraction with an increase in loading pressure. Figure 6 gives the results for the effect of loading pressure on the linear burning rate. There was a decrease in the linear burning rate with an increase in the loading pressure.

3.2 Measurement of temperature profiles

3.2.1 Effect of atmosphere pressure

Figure 7 gives the results of the effect of N_2 pressure on the burning surface temperature of the stoichiometric ratio G15B/CuO mixture. The observed surface temperature generally increased with an increase in N_2 pressure. There was also a fluctuation in observed surface temperature at approximately 2 MPa. Such tendency of fluctuation agreed with that of Sinditskii et al. [13].

Table 4 Effect of oxygen balance on the linear burning rates of G15B/CuO mixtures

Sample	Oxygen balance [g·(100 g mixture)$^{-1}$] (or [%])	a [mm·s^{-1}·MPa^{-1}]	n [−]	r [mm·s^{-1}] at 7 MPa
G15B/CuO	+5	7.42	0.264	12.40
	0	10.81	0.326	20.39
	−5	11.74	0.264	19.62
	− 10	12.67	0.342	24.65
	− 15	15.15	0.193	22.06
	− 20	15.50	0.167	21.45

* Particle size of G15B 45~75 μm
Loading pressure 9.81 MPa

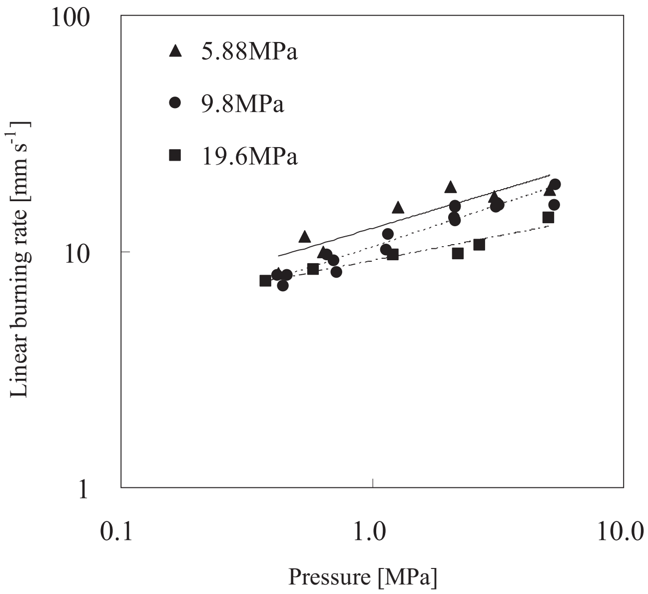

Fig. 6 Effect of loading pressure on the linear burning rates of G15B/CuO mixtures

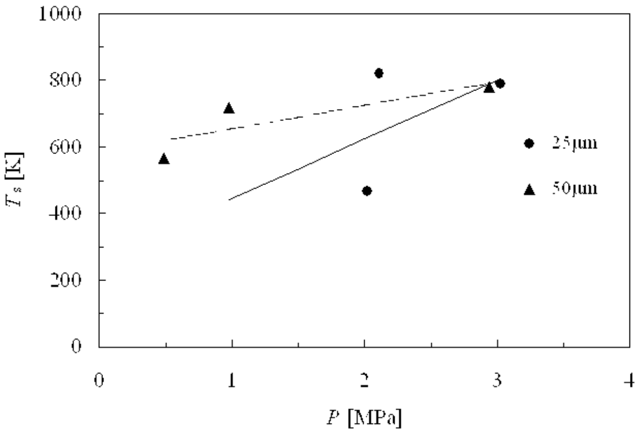

Fig. 7 Effects of atmosphere pressure and thermocouple diameter on the burning surface temperature

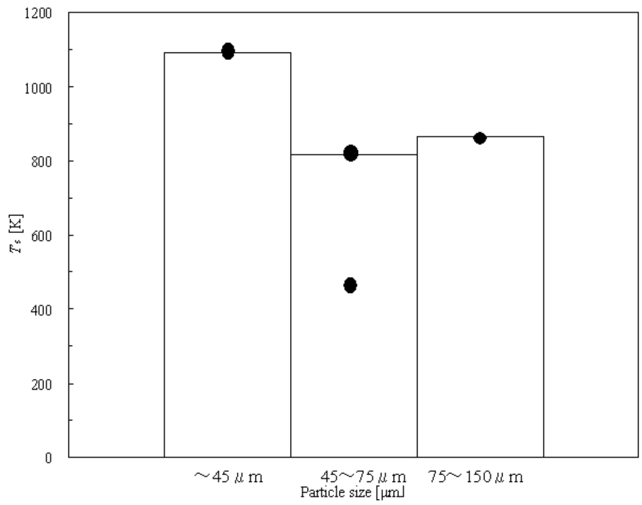

Fig. 8 Effect of G15B particle size on the burning surface temperature

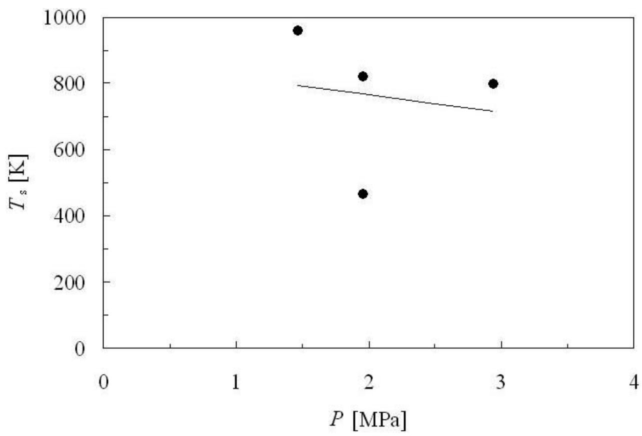

Fig. 9 Effect of loading pressure on the burning surface temperature

3.2.2 Effect of G15B particle size

Figure 8 gives the results of the effect of G15B particle size on the burning surface temperature of the stoichiometric ratio G15B/CuO mixture. The observed surface temperature generally decreased with an increase in G15B particle size.

3.2.3 Effect of loading pressure

Figure 9 gives the results of the effect of the loading pressure on the burning surface temperature of the stoichiometric ratio G15B/CuO mixture. The observed surface temperature generally decreased with an increase in loading pressure.

3.3 Suggested burning mechanism

Williams et al.[14] and Date et al.[15] have reported on the formation of melamine derivatives from cyanamides during thermal decomposition of some tetrazoles. Meanwhile, Sinditskii et al. [13] have observed the similar fluctuation in the burning surface temperature of tetrazole, as given in section 3.2.1, and they have postulated that tetrazole "burns in an unusual regime" in which "periodical build–up of a decomposition product in the surface layer" occurs, which is then "periodically removed to clean the burning surface". [13] Figure 10 gives the schematic diagrams of possible combustion mechanism of G15B/CuO mixture. It could be suggested that a similar process as that suggested by Sinditskii et al. [13] may have occured during the combustion of G15B/CuO mixture, i.e. G15B may have decomposed to periodically form melamine derivatives that melt to spread out and cover the burning surface before they are subsequently removed. This suggests that not all fuel component for the stoichiometric ratio mixture may be consumed for combustion process, which could be the reason for the maximum linear burning rate at fuel–rich region when the effect of oxygen balance was studied. The effect of G15B particle size on the linear burning rate was not obvious probably because G15B itself or its decomposition product may have melted to spread out of its original shape upon heating during the course of ignition. As for the effect of loading pressure, compression of the "gassy" sample such as G15B/CuO mixture probably makes the passage of "hot–gas" through voids of unreacted particles difficult, as shown in Fig. 11, causing a decrease in consumption of unreacted particles, i.e. the linear burning

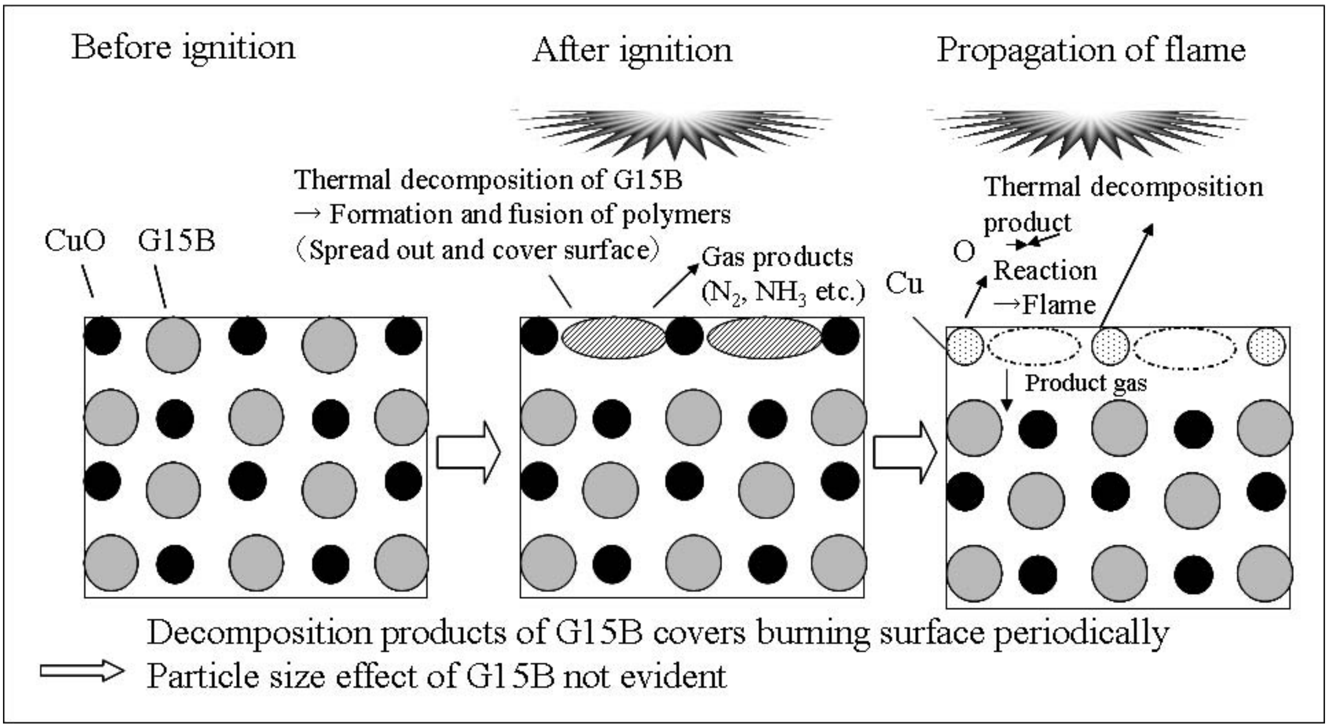

Fig.10 Possible combustion mechanism of G15B/CuO mixture

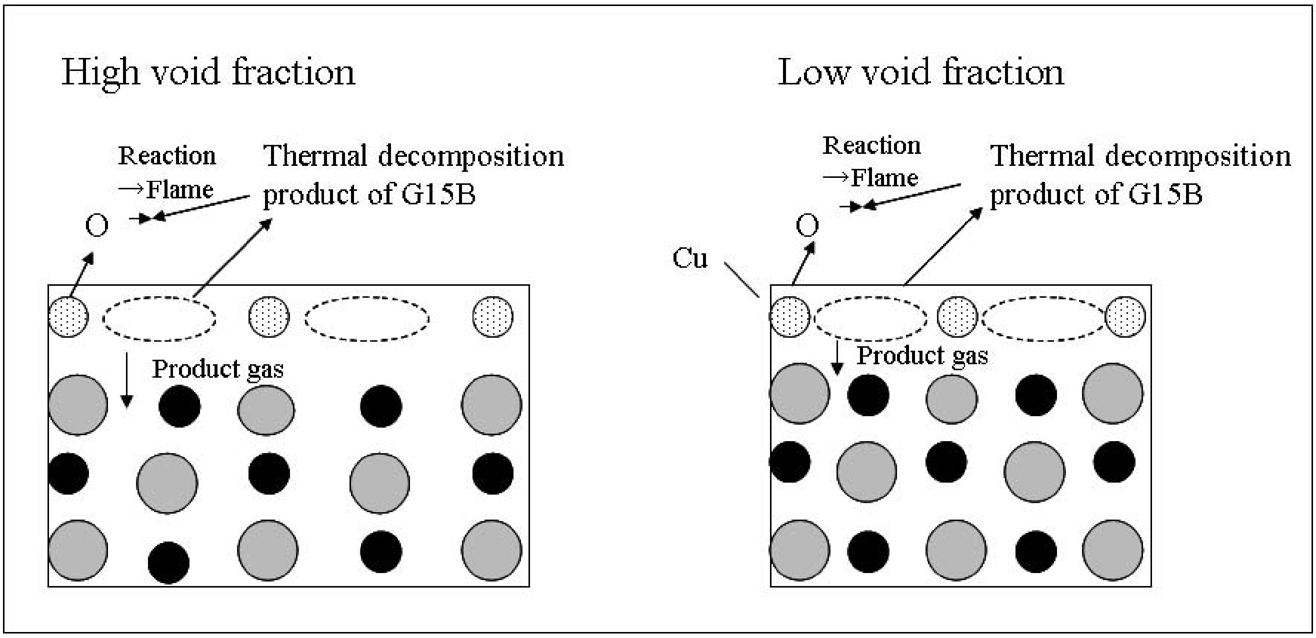

Fig.11 Possible combustion mechanism of G15B/CuO mixture-Effect of loading pressure

rate.

4. Conclusions

The combustion behavior of G15B/ CuO mixture was examined by evaluating the effects of mixing ratios of G15 B/CuO mixture, particle size of G15B and loading pressure, and also by measuring the temperature profiles of samples during linear burning rate tests. The linear burning rate reached the maximum when the oxygen balance was negative (between −15 g/(100 g mixture) ~ −20 g/(100 g mixture) (or between −15% ~ −20%)). Meanwhile, there was no noticeable effect of the particle size of G15B on the linear burning rate while there was a noticeable decrease in the linear burning rate with an increase in the loading pressure. The measurements of temperature profiles indicated that the surface temperature had significant fluctuations but generally increased with an increase in N_2 pressure. It was suggested, based on the works of Sinditskii et al., that the variation in burning surface temperature and the unapparent effect of G15B particle size on the linear burning rate may be explained by the periodical build−up of a decomposition product of G15B in the burning surface that may have occurred during the combusition of G15B/ CuO mixtures.

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1,5'−ビ−1H−テトラゾール・グアニジン塩／酸化銅(II)混合物の燃焼に関する研究

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新規ガス発生剤候補として考えられる1,5'−ビ−1H−テトラゾール・グアニジン塩（G15B）／CuO混合物の基本的な燃焼挙動について検討するため，G15B／CuO混合物の線燃焼速度に及ぼすG15B／CuO混合比の影響，量論比混合物におけるG15Bの粒径の影響および装填圧力の影響について検討を行った。また，量論比混合物の燃焼の際の温度履歴についても測定を行った。その結果，酸素バランスがマイナス(−15%と−20%の間）の場合に線燃焼速度が最大に到達することが示された。量論比混合物の線燃焼速度については，G15Bの粒径の顕著な影響が見られなかったものの，装填圧力の増加とともに線燃焼速度が減少する傾向が見られた。また，燃焼試料の温度履歴については，同じ雰囲気圧力において燃焼表面温度が変動するほか，雰囲気圧力の増大に伴い燃焼表面温度が全般的に増大する傾向が見られた。G15B過剰で線燃焼速度が最大を示したこと，量論比混合物についてG15Bの粒径の顕著な影響が見られなかったこと，そして，同じ雰囲気圧力において燃焼表面温度が変動した理由として，G15B/CuO混合物の燃焼の際にG15Bの熱分解生成物が周期的に燃焼表面において蓄積と消費が繰り返されていることが考えられる。

キーワード：1,5'−ビ−1H−テトラゾール・グアニジン塩，酸化銅（Ⅱ），燃焼挙動，線燃焼速度，温度履歴

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