Letter

A study on the burning characteristics of some guanidinium 1,5′-bis-1 H-tetrazolate / metal oxide mixtures

Shingo Date*†, Takumi Sugiyama*, Norikazu Itadzu*, Yasuyoshi Miyata*, Kazuo Iwakuma*, Masahiro Abe*, Kazuya Yoshitake*, Shizuka Nishi*, and Kazuo Hasue*

*Department of Applied Chemistry, National Defense Academy, 1-10-20 Hashirimizu, Yokosuka, Kanagawa 239-8686, JAPAN TEL+81-46-841-3810 ext. 3561 FAX+81-46-844-5901
†Corresponding address : sdate@nda.ac.jp

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Abstract

The burning characteristics of some guanidinium 1,5'-bis-1 H-tetrazolate (G 15 B)/metal oxide mixtures were examined and compared through linear burning rate tests and closed-vessel tests to evaluate the potential of the mixtures as gas generating agent for airbag inflators. The linear burning rate data of the stoichiometric ratio G 15 B/CuO mixture was higher than other mixtures that ignited including the stoichiometric ratio 5-ATZ/Sr $(NO_3)_2$ and 5-ATZ/CuO mixtures. Although the average rate-of-pressure-rise data during the closed-vessel test was over 50% lower than that of 5-ATZ/Sr $(NO_3)_2$ mixture, its average temperature-rise inside the vessel was over 80% lower than that of 5-ATZ/Sr $(NO_3)_2$ mixture. The relatively high burning rate and the low temperature-rise displayed by G 15 B/CuO mixture may suggest the highest potential as gas generating agent among some G 15 B/metal oxide mixtures studied.

Keywords : guanidinium 1,5'-bis-1 H-tetrazolate, metal oxides, gas generating agent, linear burning rate, closed vessel test

1. Introduction

Many researches and developments have been going on over the years on non-azide gas generating agents for automobile gas generating agents. Alternative fuel components of the gas generating agents studied so far include tetrazole compounds, especially 5-amino-1 H-tetrazole (5-ATZ)[1)-5)] (Fig.1)), guanidine nitrate[6),7)], nitroguanidine[6),7)] and azodicarbamide (ADCA)[8)]. Recently, Date et al. have been considering guanidinium 1,5'-bis-1 H-tetrazolate (G 15 B), which contains a double tetrazole ring as given in Fig.2, as one of the novel fuel components for gas generating agents[9)-12)]. Date et al.[9)] reported that its mixture with potassium perchlorate $KClO_4$ has demonstrated high rate of pressure rise ; superior over 5-ATZ/Sr $(NO_3)_2$ mixture, which has been used in the airbag in Japan. However, the temperature-rise during the 60 L tank test for G 15 B/$KClO_4$ mixture was up to approx. 950 K[10),11)], making it difficult for the application as gas generating agent for automobile airbag inflators. In the following study[12)], G 15 B/CuO mixtures were examined for their potential as gas generating agent through sensitivity tests and burning tests. In this study, burning characteristics of other G 15 B/metal oxide mixtures, together with some 5-ATZ/oxidizer mixtures, were examined through linear burning rate tests and closed-vessel tests, and their results were compared with the results for stoichiometric ratio G 15 B/CuO mixture[12)] and 5-ATZ/Sr $(NO_3)_2$ mixture[12)].

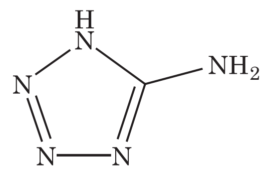

Fig. 1 Chemical structure of 5-amino-1 H-tetrazole(5-ATZ)

2. Experimental

2.1 Reagents used

G 15 B was purchased from Toyo Kasei Kogyo Co., Ltd., and 5-ATZ was purchased from Fujimoto Chemicals Co., Ltd. Some oxidizers, *i.e.* CuO (purity≧99.9%), Fe_2O_3 (purity≧99.0%) and Sr $(NO_3)_2$ (purity≧99.5%) were purchased from Kanto Chemicals Inc., Ltd. Particle sizes of G 15 B

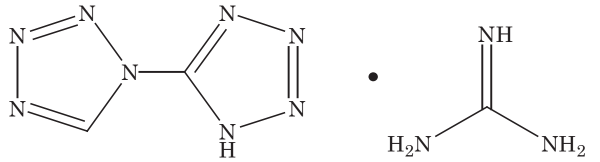

Fig. 2 Chemical structure of guanidinium 1,5'−bis−1 H−tetrazolate (G 15 B)

Table. 1 Table 1. Mixing ratios of tetrazole /oxidizer mixtures

Sample	G 15 B/ CuO[12]	G 15 B/ Fe_2O_3	G 15 B/ $Sr(NO_3)_2$	5−ATZ/ CuO	5−ATZ/ $Sr(NO_3)_2$[12]
G 15 B[wt%]	20.7	28.1	32.9	−	−
5−ATZ[wt%]	−	−	−	23.4	36.5
CuO[wt%]	79.3	−	−	76.6	−
Fe_2O_3[wt%]	−	71.9	−	−	−
$Sr(NO_3)_2$[wt%]	−	−	67.1	−	63.5

and 5−ATZ were controlled within the range of 45~75 µm, and the particle size of Sr $(NO_3)_2$ was controlled within the range of 75~150 µm, all through sieving process, but metal oxides were used without sieving. The powder reagents were then dried separately ***in vacuo*** for at least 24 hours and were then stored separately in desiccators for at least 24 hours.

2.2 Preparation of the mixtures

One of two tetrazoles, *i.e.* G 15 B or 5−ATZ, and one of oxidizers mentioned above were mixed at stoichiometric ratios as given in Table 1, by using a rotary mixer. Each mixture was then dried again separately ***in vacuo*** for at least 24 hours and it was then stored in a desiccator. With regard to the burning test data for stoichiometric ratio G 15/CuO and 5−ATZ/Sr $(NO_3)_2$ mixtures, the data of Date et al.[12] were used.

2.3 Burning test

The linear burning rate tests and the closed-vessel tests were conducted for all mixtures except for stoichiometric ratio G 15/CuO and 5−ATZ/Sr $(NO_3)_2$ mixtures, whose data of Date et al.[12] were used. The descriptions of the experimental apparatus and the methodology of the tests could be found elsewhere[12] .The closed vessel tests were conducted at least 3 times for all mixtures, and the average−rate−of−pressure−rise, $R_{av.}$, and the average temperature−rise, $(\Delta T)_{av.}$, were determined.

3. Results and discussion

3.1 Linear burning rate test

The results of the linear burning rate test for some stoichiometric ratio G 15 B/ oxidizer mixtures and some 5−ATZ/ oxidizer mixtures are given in Fig.3 and Table 2. Estimated linear burning rate for G 15 B/CuO at 7 MPa, as given in Table 2, was 20.39 mm s^{-1}, higher than those of other mixtures examined in this study, including 13.43 mm s^{-1} for 5−ATZ/CuO mixture and 10.50 mm s^{-1} for 5−ATZ /Sr $(NO_3)_2$ mixture. Meanwhile the pressure index, n, for G 15 B/CuO mixture was 0.326, which was higher than those of 5−ATZ/CuO and 5−ATZ/Sr $(NO_3)_2$ mixtures, *i.e.* 0.240

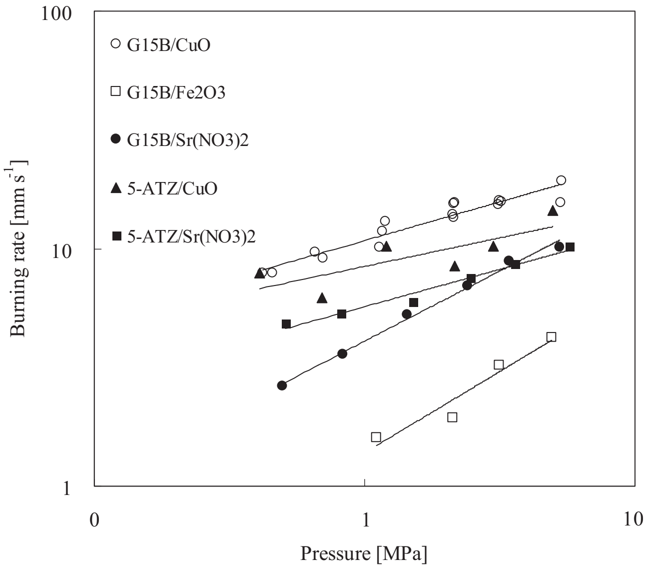

Fig. 3 Linear burning rate data for tetrazole/oxidizer mixtures

and 0.315, respectively, but lower than those of G 15 B/Fe_2O_3 and G 15 B/Sr $(NO_3)_2$ mixtures, *i.e.* 0.685 and 0.590, respectively.

3.2 Closed vessel test

The typical pressure−time curves and temperature−time curves during the closed vessel test for tetrazole/oxidizer mixtures are given in Figs.4 and 5, respectively. R_{av} and $(\Delta T)_{av}$ inside the closed vessel for tetrazole/oxidizer are given in Table 3. Although R_{av} for G 15 B/CuO mixture was over 50% lower than that of 5−ATZ/Sr $(NO_3)_2$ mixture, its $(\Delta T)_{av}$ was also over 80% lower than that of the latter mixture. Meanwhile, G 15 B/Fe_2O_3 mixture, which ignited during the linear burning rate test, did not ignite during this closed vessel test. Since the ignition method of the pellet for the closed vessel test is the same as that for the linear burning rate test (*i.e.* ignition by heated nickel/ chrome wire[12]) and that the operational pressure for the closed vessel test (*i.e.* approximately 1.96 MPa[12]) falls within the range of operational pressure for the linear burning rate test (*i.e.* within 0.3~5 MPa[12]), it could be suggested that, since the sides of a tetrazole/oxidizer mixture pellet was not coated with epoxy resin restrictor during the closed vessel test, heat energy supplied by the nickel−chrome wire to the top surface of the mixture pellet during ignition may have dissipated more readily into He atmosphere as compared to the coated pellet that was used during the linear burning rate test where heat may only have dissipated mainly from the top surface of the pellet into N_2 atmosphere, so that during the closed vessel test, there may not have been enough heat energy supplied to ignite G 15 B/Fe_2O_3 mixture pellet.

4. Conclusion

Linear burning rate tests and closed vessel tests for some G 15 B/metal oxide mixtures were conducted and their results were compared to examine the potential of the mixtures as novel gas generating agent for airbag inflators. Among some G 15 B/metal oxides mixtures exam-

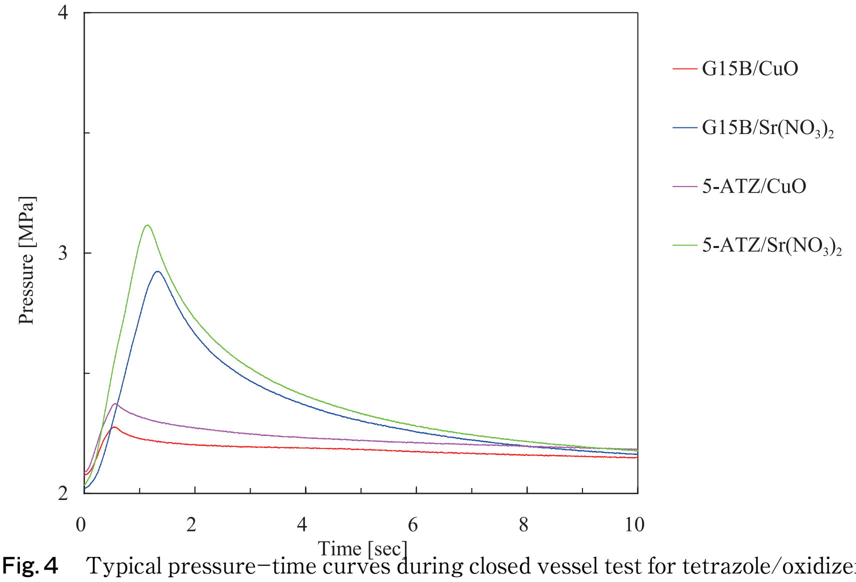

Fig. 4 Typical pressure–time curves during closed vessel test for tetrazole/oxidizer mixtures

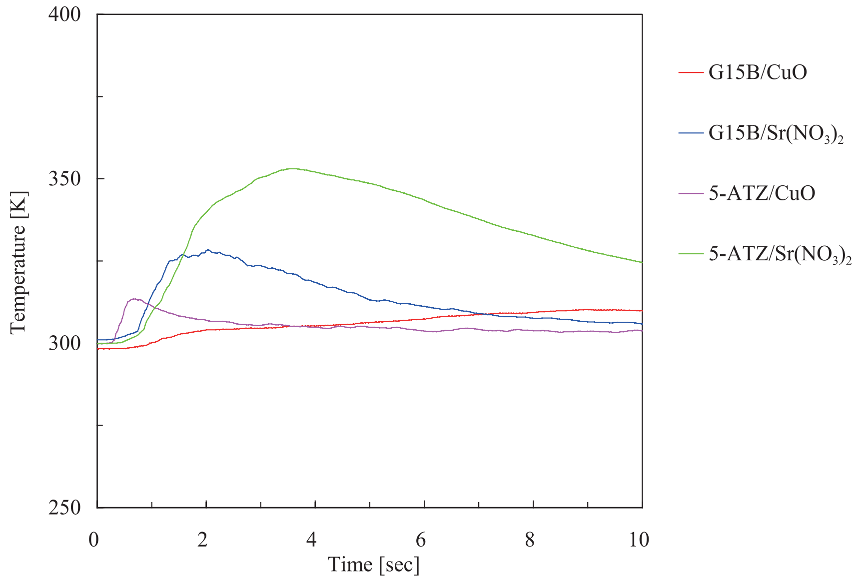

Fig. 5 Typical temperature–time curves during closed vessel test for tetrazole/oxidizer mixtures

Table. 2 Linear burning rate data for tetrazole/oxidizer mixtures

Sample	a [mm·s^{-1}·MPa^{-1}]	n [–]	r [mm·s^{-1}] at 7 MPa
G 15 B/CuO [12]	10.81	0.326	20.39
G 15 B/Fe_2O_3	1.38	0.685	5.23
G 15 B/$Sr(NO_3)_2$	4.08	0.590	12.86
5–ATZ/CuO	8.42	0.240	13.43
5–ATZ/$Sr(NO_3)_2$ [12]	5.69	0.315	10.50

Table. 3 Results of closed vessel tests for tetrazole/oxidizer mixtures

Sample	R_{av} [MPa s^{-1}]	$(\Delta T)_{av}$ [K]
G 15 B/CuO [12]	0.396	9.7
G 15 B/Fe_2O_3	NA	NA
G 15 B/$Sr(NO_3)_2$	0.736	26.1
5–ATZ/CuO	0.552	8.6
5–ATZ/$Sr(NO_3)_2$ [12]	0.838	71.4

ined in this study, the relatively high burning rate and the low temperature–rise displayed by G 15 B/CuO mixture may suggest its highest potential as gas generating agent.

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1,5'－ビ－1H－テトラゾール・グアニジン塩／金属酸化物混合物の燃焼特性に関する研究

伊達新吾*†，杉山　匠*，板津徳一*，宮田泰好*，岩隈一生*，阿部雅浩*，吉武和哉*，西　志都香*，蓮江和夫*

1, 5'－ビ－1H－テトラゾール・グアニジン塩 (G15B) ／金属酸化物混合物のエアバッグ展開用ガス発生剤としての可能性について検討するため，線燃焼速度試験及び密閉容器試験により燃焼特性について比較検討した。比較検討した混合物の中で，化学量論比の G15B/CuO の線燃焼速度が最も速く，5－ATZ/Sr $(NO_3)_2$及び5－ATZ/CuO と比較しても速いことが分かった。密閉容器試験では，化学量論比の G15B/CuO の平均圧力上昇速度が5－ATZ/Sr $(NO_3)_2$よりも50％以上低いが，平均温度上昇分が80％以上低くなることが示された。G15B/CuO は線燃焼速度が比較的速く，密閉容器試験において温度上昇が比較的低いことから，検討した G15B／金属酸化物混合物の中でガス発生剤として最も高い可能性があると思われる。

*防衛大学校応用科学群応用化学科　〒239-8686　神奈川県横須賀市走水1-10-20
TEL 046-841-3810　内線3561　FAX 046-844-5901
†Corresponding address：sdate@nda.ac.jp