Research paper

Burning performances of some guanidinium 1,5′-bis-1H-tetrazolate/ammonium nitrate/additive mixtures

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Abstract

Linear burning rates (r) and rates-of-pressure rise were measured for some guanidinium 1,5'-bis-1H-tetrazolate (G15B)/ammonium nitrate (AN)/additive mixtures in which the additive tested was one of : manganese dioxide MnO_2, copper Cu, copper (Ⅰ) oxide Cu_2O, copper (Ⅱ) oxide CuO, basic cupric nitrate (BCN), copper phthalocyanine (CuPc), activated carbon (AC), sodium nitrate (NaCl), chromium oxide (Cr_2O_3) or silicon oxide SiO_2. Linear burning rate test results show that all the additives tested enhanced the ignition of the stoichiometric ratio G15B/AN mixture, which by itself did not burn even under N_2 atmosphere at an initial gauge pressure of 10 MPa at 298 K, and that the mixture with AC or CuO additive was faster in r than the commercialized guanidine nitrate (GN)/strontium nitrate (SrN)/BCN mixture under the whole pressure range that was tested (0.1-10 MPa (initial gauge pressure)) while the mixture with Cu, Cu_2O, BCN or NaCl additive was faster under average absolute pressure over 5 MPa. As for the rate-of-pressure-rise test, all mixtures with one of the additives burnt completely three times out of three tests and that the mixture with Cu, Cu_2O, CuO or BCN additive was, although higher in the average temperature-rise, also higher in both the average pressure-rise and the average rate-of-pressure-rise, while the mixture with AC additive was higher in both the average pressure-rise and the average rate-of-pressure-rise and lower in the average temperature-rise.

Keywords : guanidinium 1,5'-bis-1H-tetrazolate, ammonium nitrate, linear burning rate, rate-of-pressure-rise, temperature-rise

1. Introduction

There have been active researches and developments regarding ammonium nitrate (AN) based clean gas generating agents, over the years, for automobile airbag inflators. Kumasaki et al.[1] have found that Cu-1H-tetrazole complex ($[Cu(CHN_4)_2]\cdot H_2O$)/AN mixture demonstrated higher pressure-rise and maximum rate of pressure rise during 52 mL deflagration test as compared to 1H-tetrazole/AN mixture. Miyata et al.[2),3)] used aminoguanidinium 5,5'-azobis-1H-tetrazolate (AGAT), a tetrazole which undergoes exothermic self-decomposition, as a fuel component, and by adding 5 wt% Cu or CuO to AGAT/AN mixture (mixed at 50 : 50 ratio), improved the mass burning rate and the average rate-of-pressure-rise, while the addition of 5 wt% MnO_2 did not show any such improvement. More recently, there have been studies on burning characteristics of guanidine nitrate /AN/BCN mixtures[4)], carbon /AN based mixtures[5)], and azodicarboamide (ADCA)/AN/CuO mixtures[6),7)]. In this study, a tetrazole compound, i.e. guanidinium 1,5'-bis-1H-tetrazolate (G15B), a double-ring tetrazole compound whose mixtures with potassium perchlorate[8)] and metal oxides[9)] have shown high performances in linear burning rates, was selected as a fuel, and the burning performances of G15B/AN/additive mixtures, in which the additive is one of Cu-based additives, i.e. copper Cu, copper (Ⅰ) oxide Cu_2O, copper (Ⅱ) oxide CuO, basic cupric nitrate (BCN) or copper phthalocyanine (CuPc) ; MnO_2

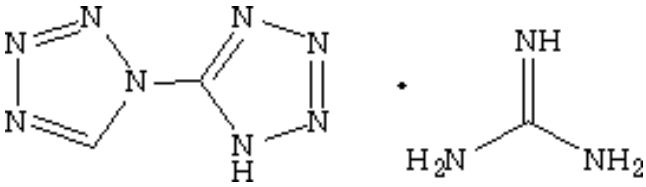

Figure 1 Guanidinium 1,5'-bis-1H-tetrazolate (G15B).

which was reported by Miyata et al.[2),3)] to be ineffective as burning catalyst of AGAT/AN based mixture but is known to accelerate thermal decomposition of AN[10)]; activated carbon (AC) (which has been found to enhance combustion of AN-based propellants[11)]), sodium chloride (NaCl) (which has been found to enhance combustion of AN-based propellants [11)]) or silicon dioxide (SiO_2)(whose amorphous state (glass) particles have been found to sensitize high explosives[10)]), were examined through linear burning rate tests and rate-of-pressure-rise tests, comparing also with GN/strontium nitrate (SrN)/BCN mixture which is used commercially for gas generating agents for automobile airbag inflators.

2. Experimental

2.1 Reagents

G15B was purchased from Toyo Chemicals Co., Ltd. AC, AN (purity : 99.0%), Cu_2O (purity : 99.0%), CuO (purity : 99.9%), SrN (purity : 99.5%), NaCl (purity 99.9%) and Cr_2O_3 (purity : ≧ 98.5%) were purchased from Kanto Chemicals Co., Ltd. Cu (purity 99.9%, average particle size 10 μm) was purchased from Rare Metallic Co., Ltd. GN was purchased from Alfa Aesar. BCN was purchased from Nihon Kagaku Sangyo Co., Ltd. Copper phthalocyanine (CuPc) (purity ≈ 95%) was purchased from Acros Organics BVBA. Particle size of G15B and GN were controlled between 45-75 μm, and the particle size of AN, NaCl and SrN were controlled between 75-149 μm, each of them through milling and sieving process, but Cu, Cu_2O, CuO and BCN were used without sieving. The powders were then dried separately under reduced pressure for a day at room temperature and they were then stored in desiccators for at least a day.

2.2 Preparation of the Mixtures and the Pellets

G15B, AN and additives were mixed at one of the mixing ratios as given in Table 1, by using a V-shaped rotating mixer. Meanwhile, as a reference mixture, GN/SrN/BCN mixture based on patented composition[12)] was prepared, mixing at a ratio of 56.05 wt% / 19.45 wt%/ 24.50 wt%. The mixtures were then dried again under reduced pressure for a day at room temperature and they were then stored in desiccators. Approximately 4 g of each dried mixture was pressed by a hydraulic press at 190 MPa for 1 minute to make a pellet (diameter 14.8 mm), to be used for the linear burning rate test or the rate-of-pressure-rise test.

2.3 Linear Burning Rate Test

The schematic diagram and the snapshot of the strand burning test apparatus are shown in Figure 2. Chimney-type strand burner TDK-15011 (Tohata Denshi Co., Ltd.) was used in this study. A pellet, previously coated with Cemedine C adhesive (Cemedine Co., Ltd.) and dried in order to achieve end-burning of the pellet that is necessary for measuring linear burning rate, was put on a strand holder and the ignition of the pellet was carried out through nickel/chrome wire (diameter 0.6 mm) in N_2 atmosphere. The internal pressure of the vessel was monitored through PG-100KU-F (Kyowa Dengyo, Co. Ltd.) strain-gauge pressure sensor, and after amplification through CDV-230C signal conditioner (Kyowa Dengyo, Co. Ltd), the signal was recorded on a data recorder (GR-3000, Keyence, Corp.). Initial gauge pressure of N_2 atmosphere was controlled between 0.1-10 MPa, and the temperature of the thermostat bath which houses the chamber was designated at 298 K. The time of the onset of pressure-rise (t_{init}) and the time of peak pressure (t_{peak}) were measured to deduce the time difference, hence the linear burning rate (r) of the pellet (length L [mm])) was calculated according to the following equations :

Table 1 Mixing ratios of G15B/AN/additive mixtures and GN/SrN/BCN mixture (units in wt.%).

Sample	G15B/AN	+MnO_2	+Cu	+Cu_2O	+CuO	+BCN	+CuPc	+AC	+NaCl	+Cr_2O_3	+SiO_2	GN/SrN/BCN
G15B	20.59	20.59	20.59	20.59	20.59	20.59	20.59	20.59	20.59	20.59	20.59	—
GN	—	—	—	—	—	—	—	—	—	—	—	56.05
AN	79.41	79.41	79.41	79.41	79.41	79.41	79.41	79.41	79.41	79.41	79.41	—
SrN	—	—	—	—	—	—	—	—	—	—	—	19.45
MnO_2	—	5.00	—	—	—	—	—	—	—	—	—	—
Cu	—	—	5.00	—	—	—	—	—	—	—	—	—
Cu_2O	—	—	—	5.00	—	—	—	—	—	—	—	—
CuO	—	—	—	—	5.00	—	—	—	—	—	—	—
BCN	—	—	—	—	—	5.00	—	—	—	—	—	—
CuPc	—	—	—	—	—	—	5.00	—	—	—	—	24.50
AC	—	—	—	—	—	—	—	5.00	—	—	—	—
NaCl	—	—	—	—	—	—	—	—	5.00	—	—	—
Cr_2O_3	—	—	—	—	—	—	—	—	—	5.00	—	—
SiO_2	—	—	—	—	—	—	—	—	—	—	5.00	—

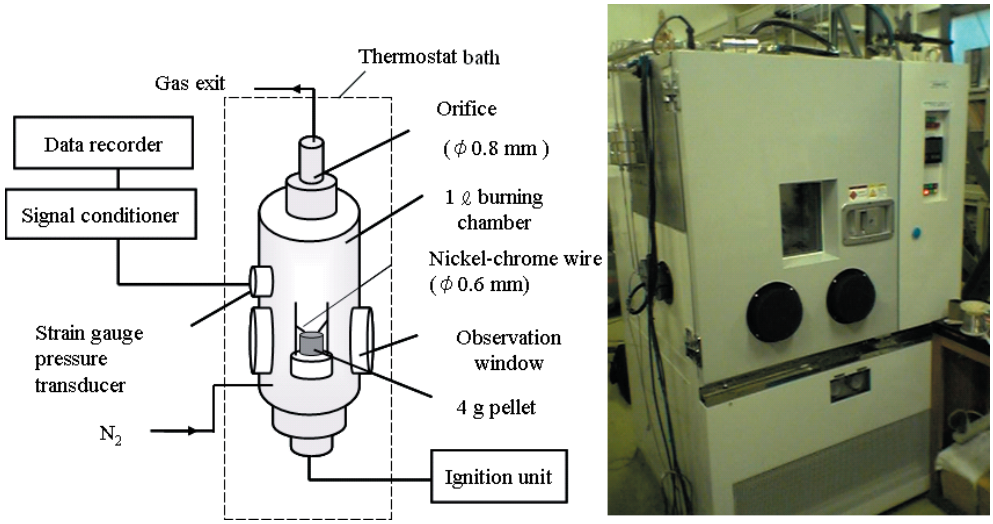

Figure 2 Schematic diagram and snapshot of strand burning test apparatus.

$$\Delta t = t_{peak} - t_{init} \quad [s] \quad (1)$$

$$r = L/\Delta t \quad [mm\ s^{-1}] \quad (2)$$

2.4 Rate-of-pressure-rise test

The same strand burning test apparatus, as shown in Figure 2, was used for the rate-of-pressure-rise test. However, unlike the linear burning rate measurement, the pellet was not coated with any adhesive, in order to achieve side burning of the pellet that occurs in gas generation agent pellets inside combustion chamber during deployment of an airbag. After inserting the strand holder with the pellet into the vessel, the atmosphere inside the strand burner was purged twice through a repetition of pressurizing N_2 gas up to gauge pressure of 0.5 MPa and releasing the purge gas through an exhaust valve. Closing the valve after completing the purging process, N_2 gas was introduced into the vessel until the internal gauge pressure reached 2.0 MPa. Upon stabilization of the internal pressure, the pellet was ignited by heated nickel-chrome wire.

The schematic diagram of the pressure-time characteristic within the chimney-type strand burner for a pellet of a given mixture is given in Figure 3. The pressure rise, ΔP, is given by

$$\Delta P = P_{peak} - P_{init} \quad [MPa] \quad (3)$$

The time difference between the onset of pressure rise and the peak pressure, Δt, is given by

$$\Delta t = t_{peak} - t_{init} \quad [s] \quad (4)$$

From (1) and (2), the average rate of pressure rise, $(\Delta P/\Delta t)$ is given by

$$(\Delta P/\Delta t) = \Delta P/\Delta t \quad [MPa\ s^{-1}g^{-1}] \quad (5)$$

Temperature-rise inside the vessel was also measured during the burning test, through K-type thermocouple (diameter 0.5 mm). Temperature-rise inside the vessel, ΔT, was determined through the following equation :

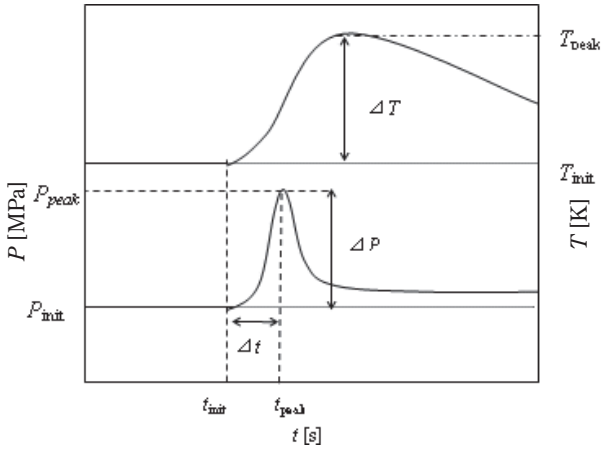

Figure 3 Schematic diagram of the change in pressure and temperature inside the closed vessel.

$$\Delta T = T_{peak} - T_{init} \quad [K] \quad (6)$$

The rate-of-pressure-rise tests were conducted 3 times each for all mixtures, and the extent of pressure rise, $(\Delta P)_{av}$, average rate-of-pressure-rise, $(\Delta P/\Delta t)_{av}$, and average temperature-rise, $(\Delta T)_{av}$, for each mixture were determined.

3. Results and discussion

3.1 Linear burning rate test

The results of the linear burning rate test for G15B/AN /additive mixtures and GN/SrN/ BCN mixture are given in Figure 4. Stoichiometric ratio G15B/AN mixture did not burn even under an initial N_2 gauge pressure of 10 MPa, but all G15B/AN/additive mixtures burnt completely at an initial gauge pressure of 2.0 MPa or above. Especially, G 15B/AN based mixtures with copper compound, *i.e.* Cu, Cu_2O, CuO, BCN or CuPc, burnt completely at an initial gauge pressure of 0.1 MPa or above. It was also found that, contrary to the finding of Miyata et al.[2),3)], addition of MnO_2, which has been known to accelerate the decomposition of AN[10)], enhanced the combustion of G15B/ AN mixture, and that the enhancement of combustion of G 15B/AN mixture through addition of AC or NaCl agreed

Table 2 Linear burning rate data for G15B/AN/additive mixtures and GN/SrN/BCN mixture.

Mixture	a [mm s^{-1}MPa^{-1}]	n [−]	r at 2MPa	r at 5MPa	r at 7MPa
G15B/AN	NA	NA	NA	NA	NA
G15B/AN/MnO_2	0.48	1.03	0.98	2.52	3.56
G15B/AN/Cu	1.71	0.93	3.26	7.64	10.45
G15B/AN/Cu_2O	2.05	0.94	3.93	9.31	12.77
G15B/AN/CuO	3.28	0.56	4.84	8.08	9.75
G15B/AN/BCN	2.02	0.89	3.74	8.46	11.42
G15B/AN/CuPc	1.41	0.80	2.45	5.11	6.69
G15B/AN/AC	2.40	0.78	4.12	8.42	10.95
G15B/AN/NaCl	1.49	1.09	3.17	8.61	12.43
G15B/AN/Cr_2O_3	1.07	0.87	1.96	4.34	5.82
G15B/AN/SiO_2	0.76	0.97	1.49	3.62	5.02
GN/SrN/BCN	2.23	0.57	3.31	5.58	6.76

NA ⋯ Did not burn, therefore data is not available.

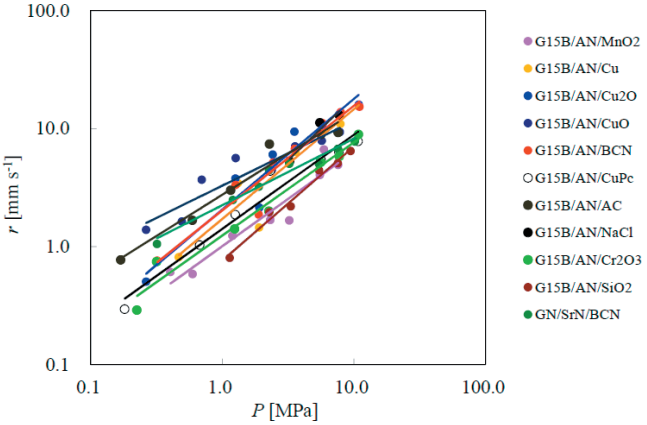

Figure 4 Linear burning rate data for G15B/AN/additive mixtures and GN/SrN/BCN mixture.

well with the finding of Sinditskii et al.[11]. The enhancement of combustion of G15B/AN mixtures through these above compounds could be due to enhancement of decomposition reaction of AN in the condensed phase[2),3)]. Meanwhile, addition of SiO_2 was also found to enhance the combustion of G15B/AN mixture, but in this case, the enhancement may be caused by the formation of hot spots through heating of SiO_2, similar to the formation of hot spots in explosives with the addition of foreign particles[10]. r of all mixtures followed Vieille's equation $r = aP^n$, where a is the pre-exponential factor, P is the average chamber (absolute) pressure, and n is the pressure index. The experimentally deduced values of a and n, together with calculated r at 2 MPa, 5 MPa and 7 MPa are given in Table 3. It was shown that, n for G15B/AN based mixture with Cu, Cu_2O or BCN was equivalent ($n \approx 0.9$), n for G15B/AN based mixture with MnO_2, NaCl or SiO_2 was equivalent ($n \approx 1.0$), while n for G15B/AN/CuO mixture was equivalent ($n = 0.56$) to that of GN/SrN/BCN ($n = 0.565$). With regard to r, it was shown that, all G15B/AN/copper compound additive mixtures except G15B/AN/Cu mixture and G15B/AN/CuPc mixture were faster than GN/SrN/BCN mixture at 2 MPa, and that all of the mixtures except G15B/AN/MnO_2 mixture, G15B/AN/CuPc mixture, G15B/AN/Cr_2O_3 mixture and G15B/AN/SiO_2 mixture were faster at 7 MPa or above. In fact, mixture with AC or CuO additive was faster than GN/SrN/BCN mixture in the linear burning rate under the whole pressure range that was tested (0.1-10 MPa (initial gauge pressure)). It was also shown that r for G15B/AN based mixture with AC, Cu, Cu_2O, BCN or NaCl was, although slower than G15B/AN/CuO mixture at 2 MPa, faster at 5 MPa for all former mixtures except G15B/AN/Cu mixture and faster at 7 MPa or above for all former mixtures.

Table 3 Rate-of-pressure-rise test data for G15B/AN/additive mixtures and GN/SrN/BCN mixture.

Mixture	$(\Delta P)_{ave}$ [MPa]	$(\Delta P/\Delta t)_{ave}$ [MPa s^{-1}]	$(\Delta T)_{ave}$[K]
G15B/AN	0.585*	0.108*	33.0*
G15B/AN/MnO_2	0.552	0.108	37.5
G15B/AN/Cu	0.544	0.249	43.6
G15B/AN/Cu_2O	0.641	0.239	29.8
G15B/AN/CuO	0.671	0.245	44.2
G15B/AN/BCN	0.682	0.298	31.1
G15B/AN/CuPc	0.598	0.134	.1.9
G15B/AN/AC	0.644	0.192	18.4
G15B/AN/NaCl	0.576	0.119	16.5
G15B/AN/Cr_2O_3	0.579	0.126	5.1
G15B/AN/SiO_2	0.343	0.078	19.7
GN/SrN/BCN	0.440	0.113	21.6

*Burnt only once

3.2 Rate-of-pressure-rise test

The result of the confined vessel test for G15B/AN/additive mixtures and GN/SrN/BCN mixture is given in Table 3. Even though the original G15B/AN mixture burnt completely only once out of each three tests, all other mixtures with additives burnt completely three times. Although the mixture with Cu, Cu_2O, CuO or BCN was higher in the average temperature-rise, they were also higher in both the average pressure-rise and the average rate-of-pressure-rise as compared to those of GN/SrN/BCN mixture, probably due to the combination of higher temperature-rise as well as an increase in the

burning rate especially for mixture with Cu_2O, CuO or BCN. Meanwhile, it was also shown that the mixture with AC additive was higher in both the average pressure-rise and the average rate-of-pressure-rise, while being lower in the average temperature-rise, probably due to an increase in the burning rate.

4. Conclusions

The effects of the addition of MnO_2, Cu, Cu_2O, CuO, BCN, CuPc, AC, NaCl, Cr_2O_3, and SiO_2 on the combustion of G15B/AN/additive mixtures were studied through linear burning rate tests and rate-of-pressure-rise tests. Addition of one of all the other additives also enhanced the combustion of G15B/AN mixture in both tests. Especially, the mixture with AC additive was faster than GN/SrN/BCN mixture in the linear burning rate under the whole pressure range tested (0.1-10 MPa (initial gauge pressure)), the mixture was higher in both the average pressure-rise and the average rate-of-pressure-rise and lower in the average temperature-rise as compared to the GN/SrN/BCN mixture for the rate-of-pressure-rise test.

References

1) M. Kumasaki, R. Miyasaka, H. Kiuchi, Y. Wada, M. Arai, and M. Tamura, Kayaku Gakkaishi (Sci. and Tech. Energetic Materials), 62, 109−116 (2001).
2) Y. Miyata, M. Abe, S. Date, M. Kohga, and K. Hasue, Sci. and Tech. Energetic Materials, 69, 117−122 (2008).
3) Y. Miyata, M. Abe, S. Date, M. Kohga, and K. Hasue, Proceedings of the Thirty-Fifth International Pyrotechnics Seminar, Fort Collins, 13−18 July 2008, IPSUSA Seminars, Inc., Marshall (2008).
4) Y. Wada, K. Hori, and M. Arai, Sci. and Tech. Energetic Materials, 71, 83−86 (2010).
5) Y. Izato, A. Miyake, and S. Date, Prop. Explos. Pyrotech., 38, 129−135 (2013).
6) K. Ikeda, Y. Shiraishi, and S. Date, Sci. and Tech. Energetic Materials, 75, 59−63 (2014).
7) K. Ikeda, A. Doi, and S. Date, Sci. and Tech. Energetic Materials, 75, 83−85 (2014).
8) S. Date, P. Boonyarat, T. Kazumi, and K. Hasue, Kayaku Gakkaishi (Sci. and Tech. Energetic Materials), 63, 209−215 (2002).
9) S. Date, T. Sugiyama, N. Itadzu, Y. Miyata, K. Iwakuma, M. Abe, K. Yoshitake, S. Nishi, and K. Hasue, Sci. and Tech. Energetic Materials, 70, 23−26 (2009)
10) H. Osada, (ed.); Explosives Chemistry, Maruzen, Tokyo (2003) (In Japanese).
11) V. P. Sinditskii, V. Y. Egorshev, A. I. Levshenkov, and V. V. Serushkin, Prop. Explos. Pyrotech., 30, 269 (2005).
12) E. Satoh, K. Ikeda, and D. Kubo, International patent WO 02/30850 A1(2002).