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Comparison of burning performances of some ammonium nitrate based mixtures with copper (II) oxide additive

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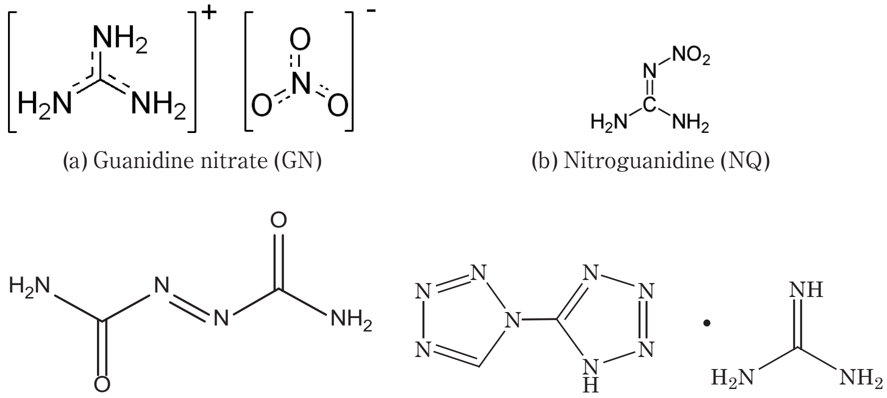
Abstract

Linear burning rates, r, and average rates-of-pressure-rise $(\Delta P/\Delta t)_{av}$, of guanidinium 1,5'-bis-1H-tetrazolate (G15B) / ammonium nitrate (AN) / copper (II) oxide (CuO) mixtures (G15B/AN/CuO 10 wt% mixture), whose percentage of CuO added to stoichiometric ratio G15B/AN mixture, and whose particle sizes of G15B and AN were different (10 wt% ; and 75 ~ 150 μm and 75 ~ 149 μm, respectively) as compared to the past study (Date et al., Sci. Tech. Ener. Mat., 76, pp. 25-29 (2015)), were measured and comparisons were made with the past results for other fuel compound/AN/CuO mixtures, where the fuel compound studied was one of : guanidine derivative compound, *i.e.* guanidine nitrate (GN) or nitroguanidine (NQ) ; or an azo compound, *i.e.* azodicarbonamide (ADCA), and also the patented guanidine nitrate (GN) / strontium nitrate (SrN) / basic copper nitrate (BCN) mixture. As a result, G15B/AN/CuO 10 wt% mixture has shown the highest r among the mixtures that were studied. It was also shown that G15B/AN/CuO 10 wt% mixture burnt readily at and above an initial gauge pressure of 0.1 MPa, similar to all mixtures except GN/AN/CuO 1 wt% and 5 wt% mixtures that were compared in this study. As for $(\Delta P/\Delta t)_{av}$, G15B/AN/CuO 10 wt% mixture has shown the highest value among all the mixtures that were compared in this study. Meanwhile, $(\Delta P/\Delta t)_{av}$ of all NQ/AN/CuO mixtures that were studied, ADCA/AN/CuO 10 wt% mixture and ADCA/AN/CuO 20 wt% mixture, together with G15B/AN/CuO 10 wt% mixture exceeded that of GN/SrN/BCN mixture.

Keywords : ammonium nitrate, guanidine derivative compound, azodicabonamide, guanidinium 1,5'-bis-1H-tetrazolate, copper (II) oxide

1. Introduction

Throughout the years, there have been researches and developments going on regarding ammonium nitrate (AN) based gas generating agents for automobile airbag inflators[1)−9)]. We have previously tested guanidine derivative compounds[5)], *i.e.* guanidine nitrate (GN) (Figure 1 (a)) and nitroguanidine (NQ) (Figure 1 (b)), azodicarbonamide (Figure 1 (c)), and guanidinium 1,5'-bis-1 H-tetrazolate (G15B) (Figure 1 (d)) as candidate fuel components, and we have selected copper(II) oxide (CuO) as one of the additives to improve burning characteristics of the AN based mixtures. In this study, burning performances of G15B/AN/CuO mixtures were measured through linear burning rate tests and rate-of-pressure-rise tests, and these results were compared with the past studies[5)−8)] for other fuel (either of GN[5)], NQ[5)] or ADCA[6), 8)])/AN/CuO mixtures, and the patented[10)] GN/ strontium nitrate (SrN)/ basic copper nitrate (BCN) mixture[5)]. Here, particle sizes of G15B and AN were standardized between 75-150 μm and 75-149 μm, respectively, and 10 parts of CuO was added to 100 parts of G15B/AN mixture, unlike the past study[9)], in order to compare burning test results with the past results[5), 6), 8)] for other fuel/AN/CuO mixtures.



(a) Guanidine nitrate (GN) (b) Nitroguanidine (NQ)

(c) Azodicarbonamide (ADCA) (d) Guanidinium 1,5'-bis-1H-tetrazolate (G15B)

Figure 1 Chemical structures of (a) guanidine nitrate, (b) nitroguanidine, (c) azodicarbonamide, and (d) guadinium 1,5'-bis-1H-tetrazolate.

2. Experimental

2.1 Sample preparation

G15B and AN were dried separately at room temperature under reduced-pressure, and they were crushed separately through separate ball mills, and subsequently sieved separately to particle size ranges between 75-150 μm and 75-149 μm, respectively. After they were mixed at stoichiometric ratio (G15B/AN : 20.59 wt%/79.41 wt%, as shown in Table 1), 10 parts by weight of dried CuO was added to 100 parts of the mixture, and the mixture were mixed mechanically through V-shaped rotating mixer. The mixing ratios of other mixtures[5),6),8)] that were compared, are shown in Table 1.

2.2 Linear burning rate test

Approximately 4 g G15B/AN/CuO mixture was pressed at 190 MPa for 1 minute by using a hydraulic press to produce a cylindrical pellet with 14.7 mm in diameter. The side surface of cylindrical pellet was coated with flame-resistant silicone sealant (TSE 3941, Momentive Performance Materials Inc.), in order to achieve end-burning that is necessary for the measurement of the linear burning rate. Linear burning rate tests were carried out for all samples in a 1 L closed strand burner[6)]. The procedures of the test could be found elsewhere[6)]. The derived linear burning rate data were compared with those of other mixtures[5),6),8)] stated above.

2.3 Rate-of-pressure-rise test

A cylindrical pellet of approximately 4 g G15B/AN/CuO mixture that was made by the same process as above without restrictor, in order to achieve side-burning of the pellet that emulates the combustion of gas generation agent pellets inside combustion chamber during deployment of an airbag, was produced and the rate-of-pressure-rise tests were carried out in the same closed strand burner as given in 2.2. The procedures of the test could be found elsewhere[6)]. The tests were conducted three times for the mixture, and the derived average-rate-of-pressure-rise data was compared with those of other mixtures that were studied previously[5),6),8)].

3. Results and discussion

3.1 Linear burning rate test

Figure 2 shows the correlations between linear burning rate, r, and average absolute pressure, $P_{\mathrm{av,ab}}$, for all the mixtures that were measured and compared[5),6),8)] in this study.

Correlations between r and $P_{\mathrm{av,ab}}$ for all the mixtures that were studied, could be approximated by equation (1),

Table 1 Mixing ratios of AN based mixtures and GN/SrN/BCN mixture (units in wt%. CuO or BCN were added to stoichiometric ratio fuel/AN mixtures).

Sample	GN/AN/CuO[5)]	NQ/AN/CuO[5)]	ADCA/AN/CuO[6),8)]	G15B/AN/CuO*	GN/SrN/BCN[5)]
GN	43.28	—	—	—	56.05
NQ	—	39.40	—	—	—
ADCA	—	—	26.6	—	—
G15B	—	—	—	20.59	—
AN	56.72	60.60	73.4	79.41	—
SrN	—	—	—	—	19.45
CuO	1, 5, 10, 20	5, 10, 20	1, 3, 5, 10, 20	10	—
BCN	—	—	—	—	24.50

*This study

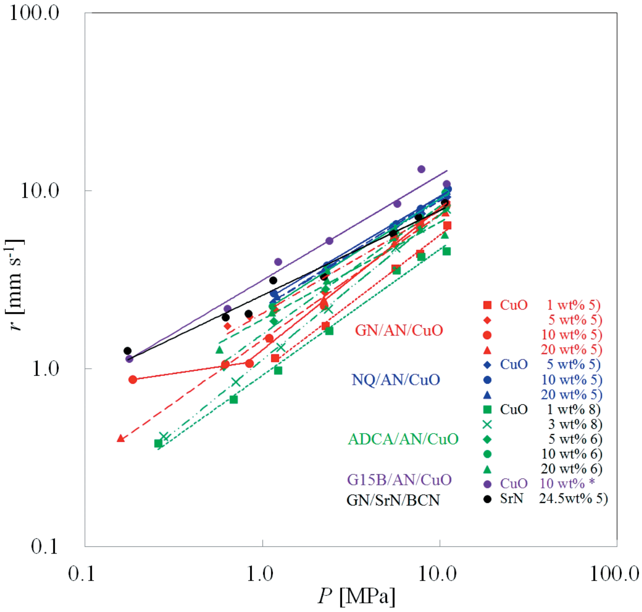


Figure 2 Linear burning rate data for AN based mixtures and GN/SrN/BCN mixture. (*denotes the set of data that were acquired in this study.)

which is known as Vieille's equation :

$$r = a \cdot P_{\mathrm{av,ab}}^{n} \tag{1}$$

where a is a pre-exponential factor and n is a pressure exponent. Table 2 shows the summary of the liner burning rate tests. G15B/AN/CuO 10 wt% mixture has shown the maximum r among all the mixtures that were studied, even exceeding that of GN/SrN/BCN mixture. Meanwhile, all AN based mixtures, except for GN/AN/CuO 10 wt% mixture at an initial gauge pressure $P_{\mathrm{init,gauge}}$ between 0.1-0.9 MPa, have exceeded in n as compared to that of GN/SrN/BCN mixture, showing higher pressure dependence of r. It was also shown that G15B/AN/CuO 10 wt% mixture burnt readily at and above $P_{\mathrm{init,gauge}}$ of 0.1 MPa, similar to all mixtures[5), 6), 8)] except GN/AN/CuO 1 wt% and 5 wt% mixtures[5)], that were compared in this study, showing good ignitability of GN/AN/CuO 10 wt% mixture.

3.2 Rate-of-pressure-rise test

Table 3 gives the summary of the rate-of-pressure-rise test for all the mixtures that were conducted and compared in this study. It was shown that among all the mixtures that were compared, G15B/AN/CuO 10 wt% mixture has shown the maximum average extent of pressure-rise, $(\Delta P)_{\mathrm{av}}$, and maximum average rate-of-pressure-rise, $(\Delta P/\Delta t)_{\mathrm{av}}$, and they exceeded those of GN/SrN/BCN mixture, while all NQ/AN/CuO mixtures[5)], together with ADCA/AN/CuO 10 wt% and 20 wt% mixtures[6)] also exceeded in $(\Delta P)_{\mathrm{av}}$ and $(\Delta P/\Delta t)_{\mathrm{av}}$ as compared to those of GN/SrN/BCN mixture.

4. Conclusions

r and $(\Delta P/\Delta t)_{\mathrm{av}}$ of G15B/AN/CuO 10 wt% mixture, whose percentage of CuO added to stoichiometric ratio G 15B/AN mixture, and whose particle sizes of G15B and AN were different as compared to the past study, were measured, and comparing with the past results for other fuel compound/AN/CuO mixtures, it was found that G15B /AN/CuO 10 wt% mixture has shown the highest r among the mixtures that were compared in this study. Meanwhile, all AN based mixtures, except for GN/AN/CuO 10 wt% mixture at $P_{\mathrm{init,gauge}}$ between 0.1-0.9 MPa, have exceeded in n as compared to that of GN/SrN/BCN mixture, showing higher pressure dependence of r. It was also shown that G15B/AN/CuO 10 wt% mixture burnt readily at and above $P_{\mathrm{init,gauge}}$ of 0.1 MPa, similar to all mixtures except GN/AN/CuO 1 wt% and 5 wt% mixtures that were compared in this study, showing good ignitability of the mixtures. As for $(\Delta P/\Delta t)_{\mathrm{av}}$, G15B/AN/CuO 10 wt% mixture has shown the highest value among all the mixtures that were studied. Meanwhile, $(\Delta P/\Delta t)_{\mathrm{av}}$ of all NQ/AN/CuO mixtures, ADCA/AN/CuO 10 wt% and 20 wt% mixtures, together with G15B/AN/CuO 10 wt % mixture exceeded that of patented GN/SrN/BCN

Table 2 Summary of linear burning rate tests for AN based mixtures and GN/SrN/BCN mixture.

Mixture		a [mm·s^{-1}·MPa^{-1}]	n [-]	$P_{\mathrm{init,gauge}}$ [MPa]	Ref.
GN/AN/CuO	1 wt %	0.97	0.76	1.0 ~ 10	5)
	5 wt %	2.05	0.58	0.5 ~ 10	5)
	10 wt %	1.11	0.15	0.1 ~ 0.9	5)
		1.28	0.80	0.9 ~ 10	5)
	20 wt %	1.39	0.72	0.1 ~ 10	5)
NQ/AN/CuO	5 wt %	2.40	0.55	0.1 ~ 10	5)
	10 wt %	2.64	0.53	0.1 ~ 10	5)
	20 wt %	2.51	0.53	0.1 ~ 10	5)
ADCA/AN/CuO	1 wt %	0.92	0.73	0.1 ~ 10	8)
	3 wt %	1.12	0.71	0.1 ~ 10	8)
	5 wt %	1.68	0.65	0.1 ~ 10	6)
	10 wt %	1.77	0.71	0.1 ~ 10	6)
	20 wt %	1.90	0.60	0.1 ~ 10	6)
G15B/AN/CuO	10 wt %	3.15	0.59	0.1 ~ 10	*
GN/SrN/BCN		2.59	0.48	0.1 ~ 10	5)

* This study

Table 3 Summary of rate-of-pressure-rise tests for AN based mixtures and GN/SrN/BCN mixture.

Sample		$(\Delta P)_{av}$[MPa]	$(\Delta P/\Delta t)_{av}$[MPa·s^{-1}]	Ref.
GN/AN/CuO	1 wt%	0.46	0.073	5)
	5 wt%	0.57	0.126	5)
	10 wt%	0.49	0.103	5)
	20 wt%	0.48	0.106	5)
NQ/AN/CuO	5 wt%	0.60	0.156	5)
	10 wt%	0.63	0.184	5)
	20 wt%	0.58	0.172	5)
ADCA/AN/CuO	1 wt%	0.46	0.055	8)
	3 wt%	0.53	0.086	8)
	5 wt%	0.54	0.123	6)
	10 wt%	0.59	0.168	6)
	20 wt%	0.56	0.152	6)
G15B/AN/CuO	10 wt%	0.77	0.322	*
GN/SrN/BCN		0.52	0.133	5)

*This study

mixture.

References

1) M. Kumasaki, R. Miyasaka, H. Kiuchi, Y. Wada, M. Arai, and M. Tamura, Kayaku Gakkaishi (Sci. Tech. Energetic Materials), 62, 109–116 (2001).
2) Y. Miyata, M. Abe, S. Date, M. Kohga, and K. Hasue, Sci. Tech. Energetic Materials, 69, 117–122 (2008).
3) Y. Wada, K. Hori, and M. Arai, Sci. Tech. Energetic Materials, 71, 83–86 (2010).
4) Y. Izato, A. Miyake, and S. Date, Prop. Explos. Pyrotech., 38, 129–135 (2013).
5) T. Otake, S. Date, K. Ikeda, and Y. Shiraishi, Sci. Tech. Energetic Materials, 76, 39–41 (2015).
6) K. Ikeda, Y. Shiraishi, and S. Date, Sci. Tech. Energetic Materials, 75, 59–63 (2014).
7) K. Ikeda, A. Doi, and S. Date, Sci. Tech. Energetic Materials, 75, 83–85 (2014).
8) K. Ikeda, Master Thesis, National Defense Academy (2014).
9) S. Date, S. Nishi, K. Asazuki, and T. Yamamoto, Sci. Tech. Energetic Materials, 76, 25–29 (2015).
10) E. Satoh, K. Ikeda, and D. Kubo, International Patent WO 02/30850 A1 (2002).