Letter

Temperature history measurements of some guanidinium 1,5′-bis-1H-tetrazolate/ ammonium nitrate/copper(II) oxide mixture

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Abstract

Temperature histories of some guanidinium 1,5′-bis-1H-tetrazolate (G15B) / ammonium nitrate (AN) / copper(II) oxide (CuO) mixture during linear burning rate tests were measured. The temperature histories, together with the estimated values of the burning surface temperature, thickness and average temperature gradient of the condensed phase zone, and temperature gradient at the burning surface for a given mixture under the same initial gauge pressure generally demonstrated variations, which may reflect the irregularities within the condensed phase zones of G15B/AN/CuO mixture. It was also shown that the estimated thickness of the condensed phase zone for G15B/AN/CuO mixture was generally thinner, the average temperature gradient within the condensed phase zone was generally greater, and the temperature gradient in the gas phase from the burning surface was generally smaller than those of stoichiometric ratio G15B /AN mixture, which suggests enhanced thermal behavior inside the condensed phase zone of G15B/AN/CuO mixture that could have caused the enhanced burning behavior of G15B/AN based mixture.

Keywords: temperature history, tetrazole, ammonium nitrate, copper(II) oxide

1. Introduction

There have been a number of researches and developments throughout the years regarding ammonium nitrate (AN) based gas generating agents for automobile airbag inflators[1)−18)]. We have been studying on the AN-based mixtures composed of guanidinium 1,5′-bis-1H-tetrazolate (G15B) (Figure 1)[4)−7), 16), 19), 20)], a double-ring tetrazole compound, as a fuel, and we have studied on G15 B／AN mixtures with various additives for the improvement of combustion characteristics. Having examined the burning characteristics of these mixtures extensively through linear burning rate tests and closed vessel tests[4)−7), 16)], we have found that manganese dioxide (MnO₂), copper (Cu), copper(I) oxide (Cu₂O), copper(II) oxide (CuO), basic copper nitrate (BCN), copper phthalocyanate (CuPc), activated carbon (AC), sodium nitrate (NaCl), chromium oxide (Cr₂O₃) and silicon dioxide (SiO₂) were shown to improve ignitability of stoichiometric ratio G15B/AN mixture, and that some copper-based additives, i.e. Cu, Cu₂O, CuO and BCN, together with AC dramatically improves the combustion characteristics of stoichiometric ratio G15B/AN mixture, exceeding linear burning rate and average rate of pressure rise of guanidine nitrate/strontium nitrate/BCN mixture[21)].

In this study, temperature histories of G15B/AN/CuO mixture, which has shown superior burning performance as shown above, were measured under different gauge
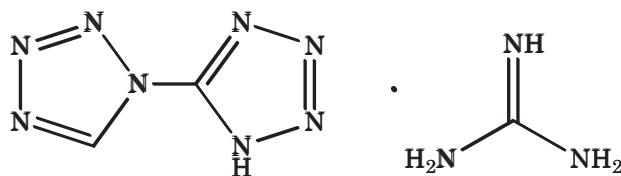
Figure 1 Chemical structure of guanidinium 1,5′-bis-1H-tetrazolate (G15B).

Table 1   Mixing ratios of G15B/AN based mixtures (units in wt%).

Sample	G15B/AN	+ CuO
G15B	20.59	20.59
AN	79.41	79.41
CuO	–	10.00

pressure to estimate the burning mechanism of the mixture.

2. Experimental
2.1 Reagents

G15B was purchased from Toyo Chemicals Co., Ltd. AN (purity: 99.0%) and CuO (purity: 99.9%; mean particle diameter: 3.3 µm) were purchased from Kanto Chemicals Co., Ltd. Particle size of G15B was controlled between 45–75 µm, and the particle size of AN was controlled between 75–149 µm; each of them through milling and sieving process, but CuO was used without sieving. The powders were then dried separately in reduced pressure for 24 hours at room temperature and they were then stored in dessicators for at least 24 hours.

2.2 Preparation of the mixtures and the pellets

Stoichimetric ratio G15B/AN (20.59 wt%/79.41 wt%) mixture, as well as G15B/AN/CuO mixture, in which 10 parts of CuO was added to 100 parts of the G15B/AN mixture, were mixed, as given in Table 1, by using a rotary mixer. The mixtures were then dried again in reduced pressure for 24 hours at room temperature and they were then stored in desiccators. Approximately 1 gram of each dried mixture, embedded with a K-type thermocouple (diameter 25 µm), was pressed by a hydraulic press at 400 MPa for 1 minute to produce a cylindrical pellet (diameter 10.5 mm) for the burning test. The surface of each pellet was then coated with adhesive bond Cemedine C (Cemedine, Co. Ltd.) and then dried, to serve as a flame retardant to ensure end-burning of the sample.

2.3 Temperature history measurement

The temperature history measurements of the mixtures were carried out by using a chimney-type strand burner TDK-15011 (Tohata Denshi Co., Ltd.). The measurement and analysis methods could be found elsewhere[7]. In this study, the initial gauge pressure of N_2 atmosphere was controlled at 1, 2 or 5 MPa, and 25 µm K-type thermocouple were used. Also, as well as the burning surface temperature T_s, the onset temperature of the condensed phase T_m and the thickness D, the average temperature gradient of the condensed phase zone ($\Delta T/\Delta x)_m$, together with the temperature gradient at the burning surface $(dT/dx)_g$, were determined using the method by Sabadell et al.[22]. The respective experimental values for each mixture and initial gauge pressure were compared with those of stoichiometric ratio G15B/AN mixture at 2 MPa.

3. Results and discussion
3.1 Measurement of temperature profiles

Figure 2 (a) gives the results on the effect of initial gauge N_2 pressure on the temperature histories of G15B/AN/CuO mixtures. It was shown that the temperature histories demonstrated different results for each initial gauge pressure, which may reflect the irregularities within the condensed phase zones of G15B/AN/additive mixtures. From the temperature inflection points of the temperature histories, as typified in Figure 2 (b), onset temperature of condensed phase zone, burning surface temperature, estimated thickness of the condensed phase zone, average temperature gradient of the condensed phase zone, and temperature gradient in the gas phase from the burning surface were estimated. Table 2 summarizes the results. Here also, there were variations in the estimated values of the burning surface temperature,
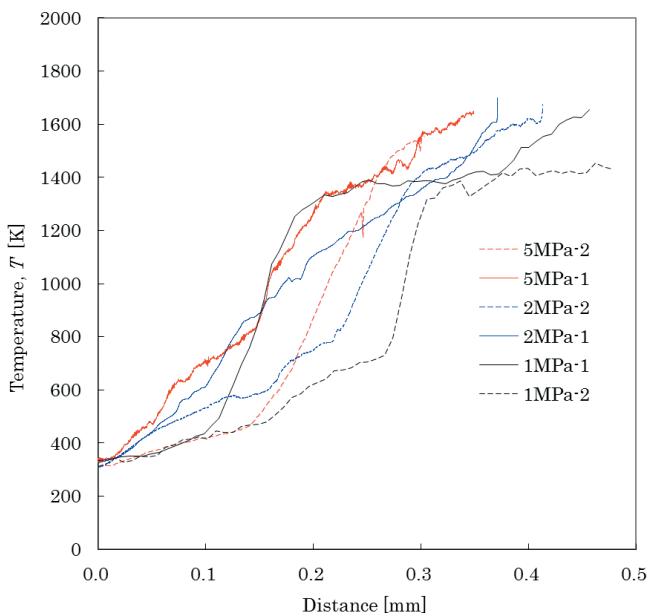
Figure 2 (a)   Temperature histories of burning G15B/AN/CuO mixture pellets.
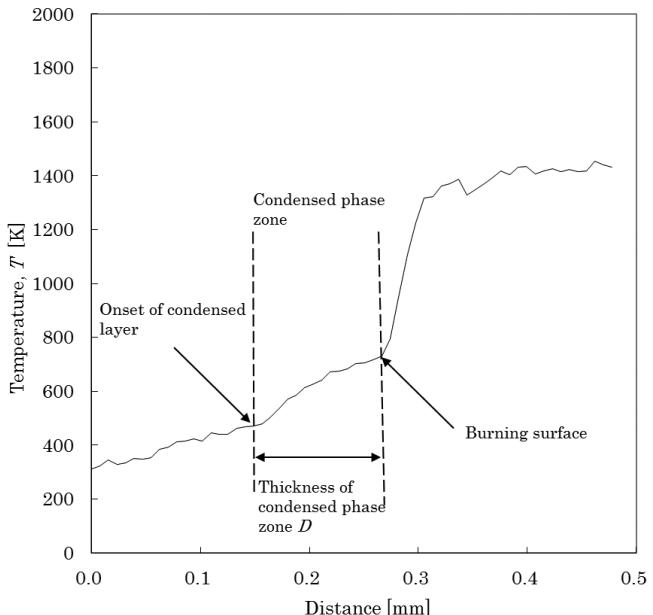
Figure 2 (b)   Typical temperature history of a burning G15B/AN/CuO mixture pellet.

Table 2   Summary of temperature history data for G15B/AN based mixtures.

Sample	P [MPa]	T_m [K]	T_s [K]	D [mm]	$(\Delta T/\Delta x)_m$ [$\times 10^3$ K mm^{-1}]	$(\mathrm{d}T/\mathrm{d}x)_g$ [$\times 10^4$ K mm^{-1}]
G15B/AN	2	465	976	0.47	1.1	2.4
+CuO	1	351	497	0.08	1.7	0.94
+CuO	1	352	732	0.23	1.7	1.2
+CuO	2	311	846	0.23	2.4	0.88
+CuO	2	317	627	0.12	2.6	0.72
+CuO	5	353	880	0.14	3.9	1.6
+CuO	5	337	479	0.12	1.2	0.56
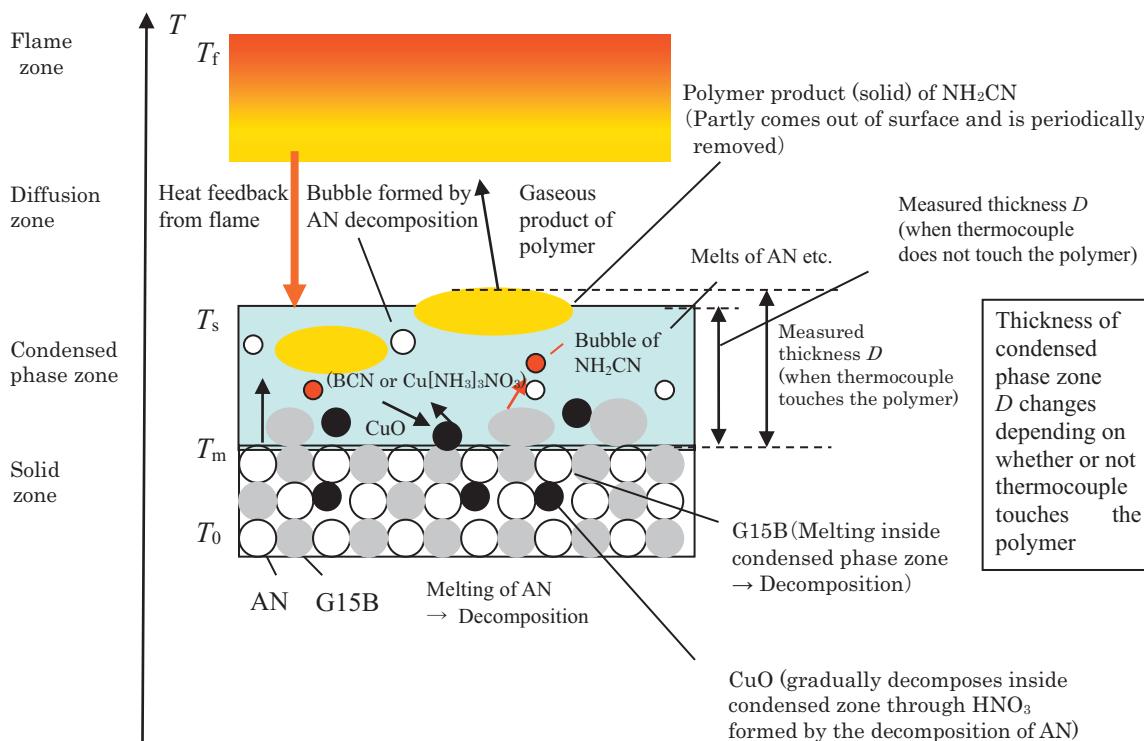
Figure 3   Estimated burning mechanism of G15B/AN/CuO mixture.

thickness and average temperature gradient of the condensed phase zone, and temperature gradient in the gas phase from the burning surface for the pressures that were studied even with the same composition that was studied twice. Such variations agreed with the results of Sinditskii et al.[23].

It was also shown that the estimated surface temperature generally increased with an increase in N_2 pressure; the estimated thickness of the condensed phase zone for G15B/AN/additive mixtures at 2 MPa were generally thinner; the average temperature gradient within the condensed phase zone were generally greater; and the temperature gradient at the burning surface were generally smaller than those of stoichiometric ratio G15B/ AN mixture, suggesting enhanced thermal behavior inside the condensed phase zone of G15B/AN/CuO mixture.

3.2 Suggested burning mechanism

Sinditskii et al.[23] have observed the similar variations in the burning surface temperature as given above in Section 3.1, 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". Date et al.[20] have suggested the similar burning mechanism for G15B/CuO mixture, where G15B may have decomposed to periodically form melamine derivatives that subsequently melted to spread out and cover the burning surface before they are removed. Figure 3 shows the estimated burning mechanism for G15B/AN/CuO mixture, involving a similar mechanism, causing variations in temperature histories, together with variations in the estimated values of the burning surface temperature, thickness and average temperature gradient of the condensed phase zone, and temperature gradient at the burning surface. It may also be possible for the formation of BCN and Cu[NH$_3$]$_3$NO$_3$ from dissolved CuO in the condensed phase in which the former is estimated to accelerate the exothermic decomposition of AN (Miyata[2], Ohtake et al.[18], Miyata et al.[24]), whose product may undergo redox reaction with decomposed gaseous product of polymers that were formed by the polymerization of G 15B decomposition product NH$_2$CN[19], thereby enhancing the burning behavior of G15B/AN based mixture.

4. Conclusions

Temperature histories of some G15B/AN/CuO mixture during linear burning rate tests that were measured in this study, together with the estimated values of the burning surface temperature, thickness and average temperature gradient of the condensed phase zone, and temperature gradient in the gas phase from the burning surface under a given composition and initial gauge pressure, have generally shown variations, suggesting that there are irregularities within the condensed phase zones of G15B/AN/CuO mixture. From the results in which the estimated thickness of the condensed phase zone for G15B/AN/CuO mixture at 2 MPa were generally thinner, the average temperature gradient within the condensed phase zone were generally greater, and the temperature gradient in the gas phase from the burning surface were generally smaller than those of stoichiometric ratio G15B/AN mixture at 2 MPa, enhanced thermal behavior inside the condensed phase zone of G15B /AN/CuO mixture was also suggested. Burning mechanism for GN/AN/CuO mixture was also estimated.

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