Research paper

Degradation mechanism of BCN in GN/BCN/water system and the effect of degradation on the thermal behavior of the system

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Abstract

Degradation decreases the quality and safety of pyrotechnic compositions. To reduce pyrotechnic degradation, a better understanding of the mechanism of degradation is required. Previously, our work revealed that exposure to water caused degradation of a guanidine nitrate (GN) and basic copper nitrate (BCN) mixture, a major component for gas-generating agents in pyrotechnics. Our previous study detected only one degradation product: copper oxide (CuO). Herein, we aim to identify other degradation products and reveal the degradation mechanism of BCN. We also study the effect of GN/BCN degradation on thermal stability. Modified accelerating aging tests and X-ray powder diffraction analysis revealed two degradation products: CuO and copper nitrate trihydrate [$Cu(NO_3)_2{\cdot}3H_2O$, CuNite]. CuNite was not observed in experiments involving heating or contact with CuO during drying. CuO was detected in each degradation. Degradation behavior in water was observed using UV-Vis spectroscopy. Quantitative spectroscopic analysis revealed a ratio of Cu^{2+} to NO_3^- of 1:2 in water during the accelerating aging test with BCN, consistent with CuNite but not with BCN. Differential thermal analysis of simulated aged GN/BCN revealed the effect of aging on thermal stability. Two degradation products, CuO and CuNite, decreased the thermal stability of GN. GN/CuO showed higher thermal stability than GN/BCN. The thermal stabilities of GN/CuO/CuNite and GN/BCN were the same, but the former showed a decrease in mass at around 100 °C due to dehydration. These results indicate thermal stability changes in GN/BCN due to aging.

Keywords: aging, degradation, basic copper nitrate, guanidine nitrate, thermal stability

1. Introduction

Basic copper nitrate [$Cu_2(NO_3)(OH)_3$, BCN] is used as an oxidizer in pyrotechnic compositions because it enhances the combustion of fuels and provides better combustion characteristics, such as significant gas production and low combustion temperature. These characteristics make BCN suitable for airbag systems. Although a mixture of guanidine nitrate [$C(NH_2)_3NO_3$, GN] and BCN (GN/BCN) has been used as a gas-generating agent[1)−6)], BCN also has been used with other materials such as ammonium nitrate[7)] and azoles[7),8)].

In airbag systems, aging is a critical safety issue. Absorption of and reaction with water can change pyrotechnic performance[9)−12)]. Recently, drivers have suffered harm from airbags during collisions; exposure of the ammonium nitrate-based gas-generating agent in the airbags to humidity resulted in compositional changes and faulty explosions[13)]. To prevent incidents such as these, a better understanding of the changes in pyrotechnic compositions and, in particular, in the gas-generating agents due to aging is essential. In our previous study[14)], we conducted accelerated aging tests for a mixture of GN

and BCN; the results revealed BCN degradation in the presence of water at 75 °C, which generated copper oxide (CuO) as a degradation product. BCN is considered a stable oxidizer. Previous papers reported that mixing GN with BCN enhanced the decomposition of BCN at temperatures over 160 °C[3), 6)]. Our previous experiments revealed that adding GN suppressed the degradation of BCN in water at 75 °C[14)]. The present study aimed to elucidate the mechanism of BCN degradation in GN/BCN in the presence of water. Thermal decomposition of the GN/BCN-based gas-generating agent was also evaluated as a function of BCN degradation.

In this study, simulated aged samples were prepared by mixing GN/BCN and CuO or copper nitrate trihydrate [$Cu(NO_3)_2 \cdot 3H_2O$, CuNite] as degradation products to be used for thermal measurements in an accelerated aging test. The degradation mechanism was characterized by X-ray powder diffraction (XRD) analysis and ultraviolet-visible (UV-Vis) spectroscopy. The effect of degradation on the thermal decomposition of GN/BCN was observed using thermogravimetry-differential thermal analysis (TG-DTA).

2. Experimental

2.1 Sample preparation

All reagents were used without further purification. Purification levels for the reagents were as follows: GN ≥ 97.0 %; BCN ≥ 99.9 %; CuNite ≥ 99.0 %; and CuO ≥ 95.0 %.

In this study, a ratio of 9:4 for GN:BCN was used based on a previous investigation[3), 6)]. Deionized water was used for all experiments.

For the accelerated aging test, BCN/water samples were prepared. The ratio of BCN/water was 0.3 g/30 mL. CuNite/water samples were prepared with 0.121 g (0.5 mmol) of CuNite/10 mL water to observe the effect of drying on CuNite.

For quantitative UV-Vis spectroscopy, standard solutions of 0.5, 5, 25, and 50 mM CuNite were prepared in volumetric flasks (100 mL).

The TG-DTA sample was prepared by mixing reagents according to the sample compositions summarized in Table 1. Aged GN/BCN samples consisted of GN and BCN with purchased copper compounds added to simulate BCN degradation products. For example, GN/CuNite was prepared to observe the effects of the BCN degradation product, CuNite, on the thermal decomposition of GN.

2.2 Aging and drying tests

The accelerated aging test was carried out in flat-bottom glass tubes (external diameter: 30 mm, length: 120 mm), as shown in Figure 1. The tubes were closed by a glass plate and the temperature was maintained at 75 °C. Samples were stirred at 300 rpm with a stirring bar. After the accelerating aging test, samples were cooled in ice water. BCN/water was treated in the same manner.

In order to obtain a solution that does not contain insoluble materials, each sample was filtered with qualitative filter paper (5 μm particle retention, Toyo Roshi Kaisha, Ltd.). The filtrate of aged samples [aged BCN (filtrate)] was dried and the residue [aged BCN (residue)] was collected and dried on a glass plate at room temperature. For reference, aged samples dried without filtration (aged BCN) were also prepared. In order to observe the effect of heating during the drying process, only the CuNite/water (75 °C) was dried at 75 °C.

2.3 Conditions for XRD

Sample powders were prepared on a glass plate and measured by XRD (SmartLab, Rigaku Corporation). Cu K

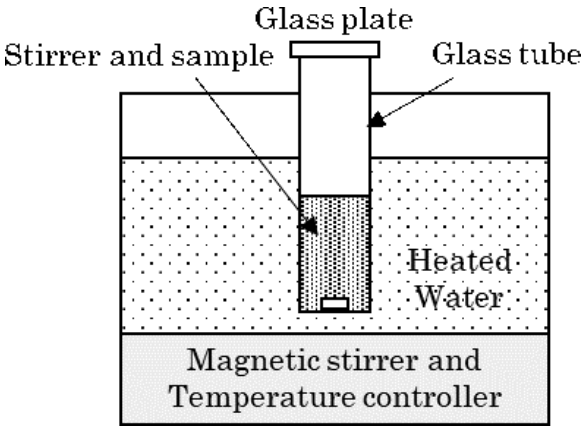

Figure 1 Schematic of accelerated aging test.

Table 1 Ratio of sample for TG-DTA.

Name	Mol ratio (Weight ratio)			
	GN	BCN	CuO	CuNite
GN/BCN	9 (1099)	4 (960.5)	–	–
Aged GN/BCN 10 % (GN/BCN/CuO)	9 (1099)	3.6 (864.4)	0.8 (63.64)	–
Aged GN/BCN 50 % (GN/BCN/CuO)	9 (1099)	2 (480.2)	4 (318.2)	–
Aged GN/BCN 100 % (GN/CuO)	9 (1099)	–	8 (636.4)	–
Aged GN/BCN 100 % (GN/CuO/CuNite)	9 (1099)	–	6 (477.3)	2 (483.2)
GN/CuNite	9 (1099)	–	–	2 (483.2)

α radiation was used at 40 kV and 45 mA. The scanning speed was 20° min^{-1} and the step width was 0.01°.

2.4 Conditions for UV-Vis

UV-Vis spectra were measured using a V-560 UV-Vis Spectrometer (JASCO). Samples were placed in a 10-mm path length quartz cell. Measurements were gathered between 200 and 900 nm with three integrations. The scanning speed was 200 nm min^{-1} with a 0.5 nm resolution and a bandwidth of 1 nm.

2.5 Conditions for TG-DTA

TG-DTA was measured on a TG-8120 Differential Thermogravimetric Analyzer (Rigaku Corporation). Samples of approximately 1.5 mg were heated in open aluminum oxide pans under nitrogen atmosphere (50 mL min^{-1}). The heating rate of the samples was 5 K min^{-1}.

3. Results and discussion

3.1 Analysis of degradation products of the BCN/water system

The XRD results of the aged BCN samples are shown in Figures 2 and 3. The XRD pattern of the aged BCN (filtrate) displays peaks matching those of CuNite. The XRD pattern of the aged BCN (residue) shows peaks derived from BCN and CuO. These results indicate that CuO and CuNite were produced by the degradation of BCN in water.

The XRD patterns of the aged, unfiltered BCN match the patterns observed for BCN and CuO. CuNite is not observed in the XRD pattern of aged BCN, whereas peaks attributed to $Cu(NO_3)_2{\cdot}3H_2O$ are found in the XRD pattern of the aged BCN (filtrate). It is possible that CuNite in aged BCN reacted to produce another substance.

A previous study reported that CuO and CuNite react in water to generate BCN[15]. If CuO and CuNite are the only products of degradation, the reversible reaction can be expressed as the following equation;

$$2Cu_2(NO_3)(OH)_3 \Leftrightarrow 3CuO + Cu(NO_3)_2{\cdot}3H_2O \quad (1)$$

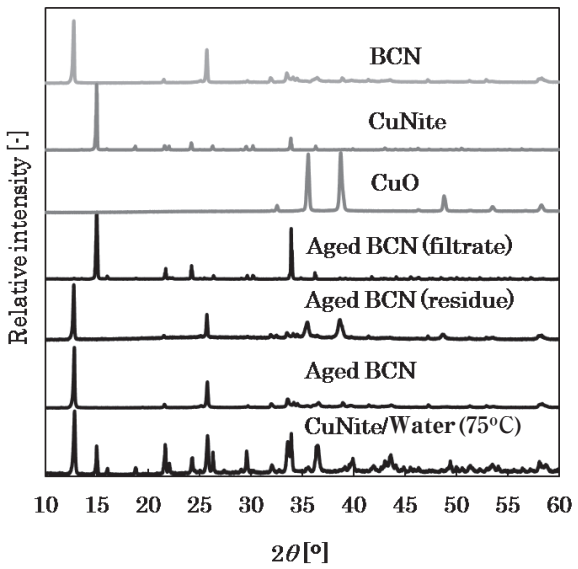

Figure 2 XRD pattern of aged BCN samples (Aging span: 2 [h]).

Additionally, according to the peaks observed in the XRD pattern for CuNite/water (75 °C), CuNite decomposes during the heating to generate BCN (Figure 2).

$$8Cu(NO_3)_2{\cdot}3H_2O \Leftrightarrow 4Cu_2(NO_3)(OH)_3 + 3O_2 + 12NO_2 + 18H_2O \quad (2)$$

From equations (1) and (2), substituting CuNite with BCN decreases the amount of CuNite and leads to increased CuO in the degradation products.

Decomposition of BCN has also been observed to generate CuO at 257 °C in vacuo[16]. The following equation represents the decomposition:

$$4Cu_2(NO_3)(OH)_3 \Leftrightarrow 8CuO + O_2 + 4NO_2 + 6H_2O \quad (3)$$

Equation (3) was derived from equations (1) and (2). Note that the degradation of BCN in water at 75 °C is the same as decomposition of BCN in vacuo.

3.2 Observation of dissociation of BCN in water

The UV-Vis spectra of aged BCN (filtrate) aqueous solutions are shown in Figure 4. The peaks of aged BCN (filtrate) at 75 °C correspond to CuNite. These peaks intensified over time.

Quantitative analysis was used to calibrate the CuNite concentration, as shown in Figure 5. The peak at 300 nm corresponds to nitrate ions (NO_3^-), whereas the peak at 800 nm corresponds to copper (II) ions (Cu^{2+})[17),18)]. The quantitative analysis of the aged BCN (filtrate) at 75 °C is shown in Figure 6. The ratio of Cu^{2+} to NO_3^- in the aged BCN (filtrate) at 75 °C remained 1:2 during the aging test. This does not match the ratio of Cu^{2+} to NO_3^- in BCN $\left(Cu^{2+} : NO_3^- = 2 : 1\right)$; rather, it matches the ratio in CuNite $\left(Cu^{2+} : NO_3^- = 1 : 2\right)$. From our experimental results, the dissociation of BCN can be expressed as the following equation:

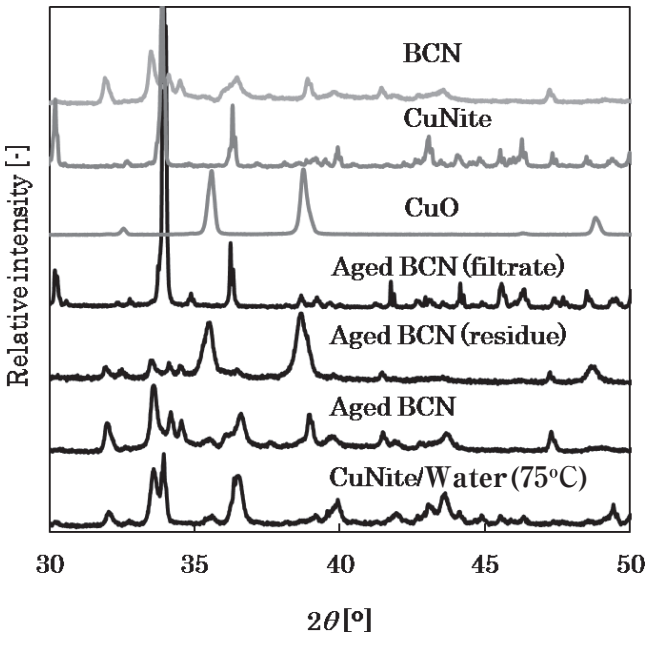

Figure 3 XRD pattern of aged BCN samples (Aging span: 2 [h]) [Enlarged around CuO peaks].

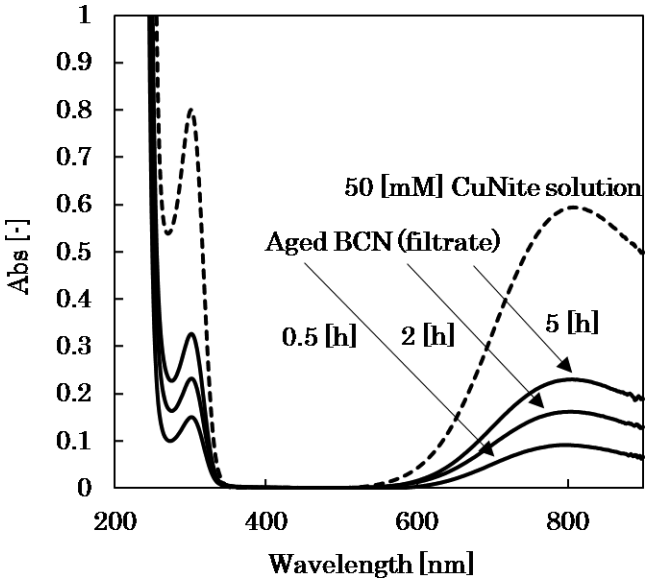

Figure 4 UV-Vis curves of aged BCN (filtrate).

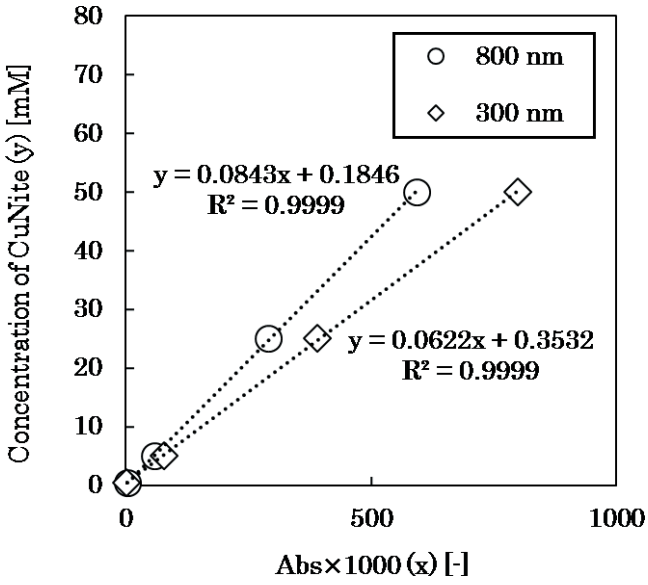

Figure 5 Calibration line of CuNite solution.

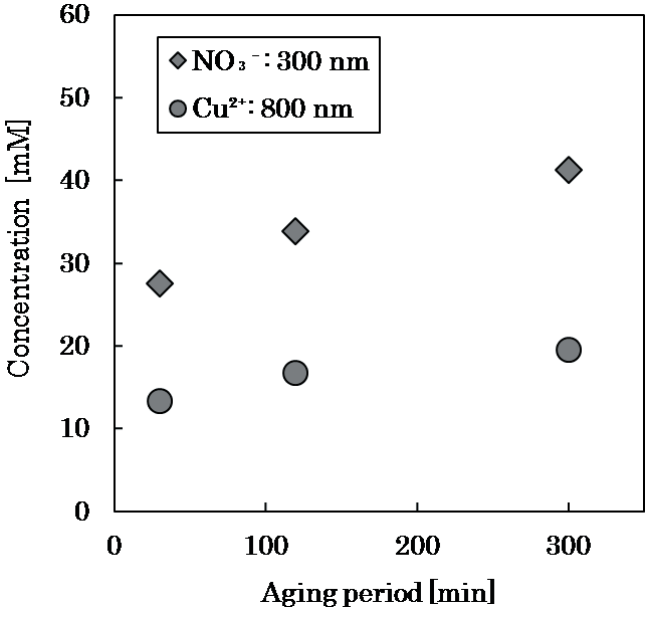

Figure 6 Quantitative analysis of Cu^{2+} and NO_3^- in aged BCN (filtrate).

$$2Cu_2(NO_3)(OH)_3 \Leftrightarrow 3CuO\downarrow + Cu^{2+} + 2NO_3^- + 3H_2O \quad (4)$$

3.3 Effect of degradation on the thermal decomposition of GN/BCN

The DTA and differential TG (DTG) curves of the aged GN/BCN are shown in Figures 7 and 8, respectively. The onset temperature (T_{onset}) and peak temperature (T_p) for the exothermic peaks of DTA and the largest decomposition peaks of DTG were calculated with Advanced Thermal Analysis Software and the results are summarized in Table 2.

The effect of CuO (a degradation product) on GN decomposition was observed in GN/CuO. GN/CuO showed an exothermic peak during weight loss. Considering weight loss, the T_{onset} value of GN/CuO was higher than that of GN/BCN. Thus, CuO may enhance the decomposition of GN because the T_{onset} value of GN/CuO was lower than that of GN. The decreased T_{onset} value produced by CuO was lower than that of BCN. These results indicate that the loss of BCN due to CuO generation increases the thermal stability of GN.

To observe the effect of the conversion of BCN to CuO, DTA and DTG curves for aged GN/BCN 10 % (GN/BCN/CuO) and aged GN/BCN 50 % (GN/BCN/CuO) were measured. Figure 7 and Table 2 indicate that the degradation had a minimal effect on the T_{onset} value for GN/BCN with 10 %, 50 %, and 100 % CuO in DTA. The T_{onset} values of GN/BCN with 10 % and 50 % conversion were the same as those of GN/BCN in DTG. From these results, the effect of CuO on the thermal stability of GN/BCN was minimal, whereas BCN had a larger effect on the thermal stability of GN.

CuNite was obtained when the degradation product was filtered. We therefore assessed the effect of CuNite on GN decomposition. Compared to GN/BCN and GN/CuO/CuNite, degradation had little influence on the thermal behavior in the DTA and DTG analyses, apart from weight loss at around 100 °C. The weight loss is likely due to dehydration of CuNite[19]. This result was different from that of GN/CuO; CuNite does not significantly change thermal stability according to the DTA and DTG curves of GN/CuNite.

4. Conclusion

Accelerating aging tests revealed that CuO and CuNite are the products of degradation of GN/BCN in water. CuNite is not stable when in contact with CuO and/or when heated. Separation of CuO and NO_3^- increased CuNite generation. Conversely, heating or contact between CuO and NO_3^- reduced the generation of CuNite.

The first step of BCN degradation in water is the dissociation of BCN, which releases Cu^{2+} and NO_3^-. The UV-Vis spectra revealed that the mole ratio of Cu^{2+} to NO_3^- was 1:2 in solution after the dissociation of BCN, matching the ratio of these ions in CuNite.

The effect of degradation on the thermal stability of GN/BCN was observed by preparing simulated aged samples. The complete conversion of BCN to CuO increased the

Table 2 T_{onset} and T_p of exothermic peaks and largest decomposition peak.

Name	DTA		DTG	
	T_{onset} [°C]	T_p [°C]	T_{onset} [°C]	T_p [°C]
GN	–	–	274	296
BCN	–	–	215	228
GN/BCN	212	219	193	216
Aged GN/BCN 10 % (GN/BCN/CuO)	210	223	193	216
Aged GN/BCN 50 % (GN/BCN/CuO)	213	218	197	216
Aged GN/BCN 100 % (GN/CuO)	212	223	235	270
Aged GN/BCN 100 % (GN/CuO/CuNite)	219	225	205	222
GN/CuNite	206	211	198	210

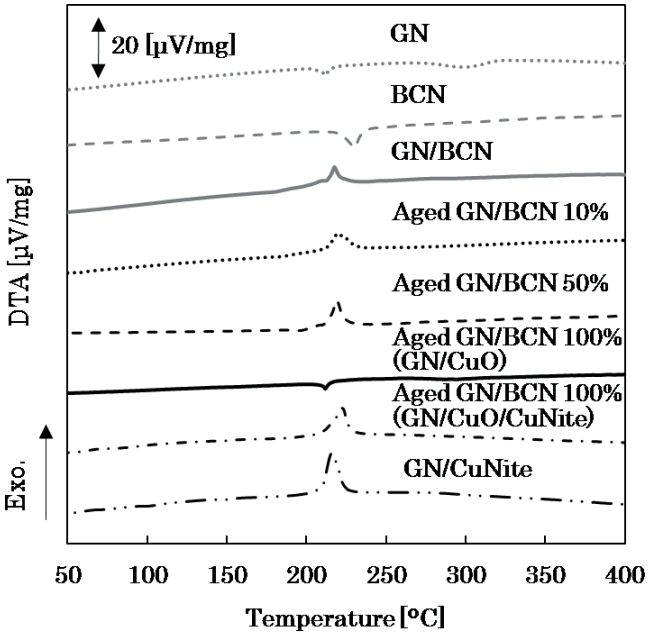

Figure 7 DTA curves.

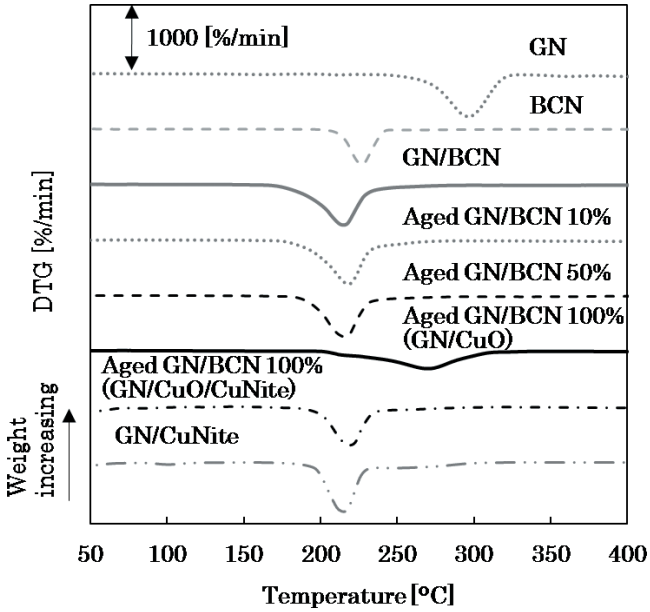

Figure 8 DTG curves.

thermal stability, whereas 10 % and 50 % conversions had little effect. Conversion of BCN to a mixture of CuO and CuNite had minimal effect on the thermal stability. Our experimental results indicate that CuNite decreases the thermal stability of GN as BCN.

In this work, we identified the products of BCN degradation and proposed an initial mechanism for BCN degradation. Gas analysis is required to elucidate the degradation mechanism completely.

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