

Combustion mechanism of mixtures of guanidine nitrate, ammonium nitrate, and basic copper nitrate

Yusuke Wada^{*†}, Keiichi Hori^{**}, and Mitsuru Arai^{***}

^{*}Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, JAPAN
TEL +81-3-5841-2980

[†]Corresponding address : yusuke.wada@aist.go.jp

^{**}Institute of Space and Astronautical Science / Japan Aerospace Exploration Agency, 3-1-1 Yoshinodai, Sagami-hara, Kanagawa 229-8510, JAPAN

^{***}Environmental Science Center, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, JAPAN

Received : January 22, 2010 Accepted : February 17, 2010

Abstract

With the aim of developing ammonium nitrate (AN) for conventional use as a new oxidizer for gas-generating agents in automobile airbag systems, the combustion characteristics of model gas-generating agents consisting of guanidine nitrate (GN), basic copper nitrate (BCN), and AN were investigated. Based on the results of strand burner tests, four conclusions were obtained : (1) the presence of BCN allows ignition of GN/AN mixtures, which do not ignite without BCN, and sustained combustion at lower pressure (about 1MPa) ; (2) the nature of the combustion residues from the GN/AN/BCN mixtures varied depending on the combustion conditions and the mixing ratio of the sample mixture ; (3) the value of the pressure exponent n was smaller (0.41-0.45) in mixtures with a high AN content or when the test was conducted under low pressure (<5MPa), but larger (0.67-0.77) in mixtures with a low AN content or when the test was conducted under high pressure (>5MPa) ; (4) the combustion wave could be divided into four regions based on the temperature and phase of the mixture. Based on these results, the model suggested for the mechanism of combustion was one in which diffusion combustion and homogeneous combustion co-exist.

Keywords : ammonium nitrate, combustion, linear burn rate

1. Introduction

Ammonium nitrate (AN) has been investigated as an alternative oxidizer component for gas generation in automobile airbag systems¹⁾. It is expected to be superior to conventional oxidizing agents, such as strontium nitrate (SrN) and basic copper nitrate (BCN), due to its low-temperature combustion, low emissions, and greater cost efficiency. However, some disadvantages, such as its ignition performance, combustion characteristics, hygroscopic characteristics, and phase transitions between solid phases, have thus far prevented AN from being developed for practical use²⁾.

Various studies have been carried out on the combustion and thermal decomposition of AN and AN mixtures^{3),4)}. Glazkova reported that the presence of water in-

terfered with the equilibrium of some elementary reversible decomposition reactions of AN⁴⁾. Brower elucidated two reaction paths for the thermal decomposition of AN⁵⁾. In this model, at lower temperatures-below 290°C-the decomposition of AN is promoted mainly by certain equilibrium reactions, and is interfered with by water or ammonia. However, at temperatures above 290°C, radical chain reactions become dominant, and the effects of water and ammonia on thermal decomposition can be eliminated. With regard to the combustion mechanism of AN-based propellants, Sinditskii recently reported that the dissociation reaction of AN into ammonia and nitric acid is rate-controlling, and the rate of this dissociation reaction is positively correlated with the temperature of the condensed phase, so the feeding of reaction heat from a side reaction,

such as a redox chain reaction between AN and potassium dichromate, is effective.^{6,7)} Despite these achievements, scientific knowledge about the combustion characteristics of AN and AN-based gas-generating agents is still lacking from the point of view of developing functional gas-generating agents. In this study, the linear burning rates and temperature profiles of various mixtures containing AN were measured using chimney-type strand burner tests, and we provide some qualitative speculation about the combustion mechanism.

2. Experimental

2.1 Samples

Samples for the combustion tests consisted of three components. Guanidine nitrate (GN, Daicel Chemical Industries, Ltd.) was used as a fuel component, AN (Daicel Chemical Industries, Ltd.) as an oxidizer, and BCN (Daicel Chemical Industries, Ltd.) as an additive. These three components were mixed in a dry system.

To prepare samples for measurement of the burning rate, 3 g of each mixture was molded and pressed into a cylindrical strand sample holder with a diameter of 9 mm and a length of about 30 mm. The side surface of the specimen was covered with epoxy resin (Cemedine Co., Ltd.) to restrict burning in that area; then, two horizontal holes was drilled perpendicularly with 10 mm intervals, and a solder wire was laced through each hole.

To prepare samples for temperature measurement, 1.5 g of each mixture was molded and pressed into a cylindrical strand sample holder of 9 mm diameter and about 15 mm length. A Π -shaped thermocouple (25 μ m diameter, R-type, Sigmund Cohn Corp.) was sandwiched between two strands, and the strands were connected with tape placed on the side surfaces. The ratios of GN to AN in the various mixtures were 20 : 80, 25 : 75, 30 : 70, 35 : 65, 40 : 60, and 50 : 50 (mass %), and the amount of BCN added was fixed at 20 parts against the sum of GN and AN. The component ratios of the test samples are shown in Table 1.

2.2 Measurement of burn rate

Strand burner tests for measuring the burn rate were carried out using a chimney-type strand burner vessel (Kyowa Giken Co., Ltd.), under a nitrogen atmosphere of 1, 3, 5, 7, or 9 MPa at room temperature (about 300 K). The

Table 1 Composition of model gas-generating agents for strand burner tests, and results obtained.

Sample	GN mass%	AN mass%	BCN equiv.*	a	n	
1	20	80	20	1.00	0.44	
2	25	75	20	1.38	0.45	
3	30	70	20	1.82	0.41	
4	35	65	20	2.74	0.41	1–5 MPa
5	35	65	20	1.46	0.77	5–9 MPa
6	40	60	20	1.60	0.74	
6	50	50	20	2.40	0.67	

* The amount of BCN is given as equivalents with respect to the total amount of GN and AN.

upper flat surface of the strand specimen was ignited by a heated nichrome wire (0.23 mm diameter). Pressure was measured through a strain-gauge pressure transducer and amplifier. The burn rate (r) was calculated from the ratio of the distance between the two solder wires and the time interval between the breaking of each solder wire, which was detected by observing the change in voltage. The average ambient pressure (P) was taken as the average of the pressure values when each solder wire was broken.

2.3 Temperature profile measurement

Strand burner tests for temperature profile measurements were carried out under a 3 MPa nitrogen atmosphere. The output from the thermocouple was recorded through a transient recorder and amplifier, and temperature-time curves were obtained.

3. Results and discussion

3.1 Burn rate

First, we attempted to investigate the combustion characteristics of samples without BCN, with component ratios of GN/AN = 30 : 70, 40 : 60, 50 : 50, and 60 : 40. However, samples without BCN were not ignited by the ignition unit. In contrast, every sample containing BCN was ignited and gave sustained combustion.

The measured and calculated values for burn rate (r) and pressure (P) were applied to equation (1), which is known as Vieille's law. The empirical formula describes the correlation between r and P ⁸⁾:

$$r = a P^n \quad (1)$$

where a is a preexponential constant and n is the pressure exponent of r . Figure 1 shows the relationship between r and P . Values of n were calculated based on this equation.

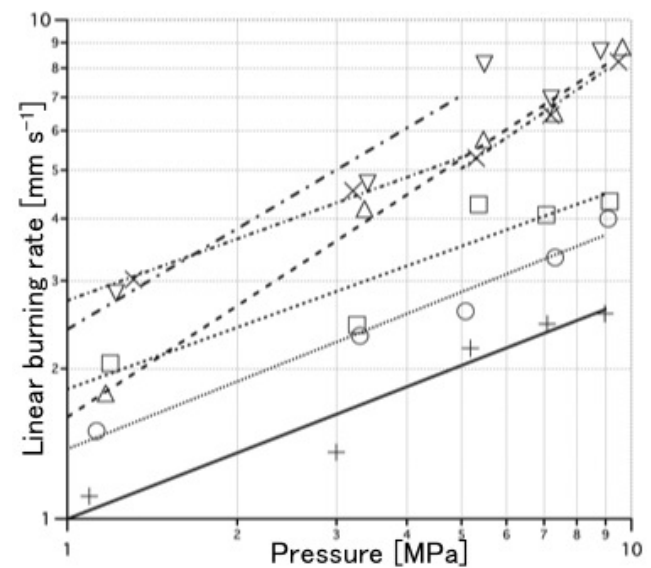


Fig. 1 Pressure dependence of burn rate for GN/AN/BCN mixtures.

- + Sample 1 (GN/AN/BCN = 20 : 80 : 20);
- sample 2 (GN/AN/BCN = 25 : 75 : 20);
- sample 3 (GN/AN/BCN = 30 : 70 : 20);
- × sample 4 (GN/AN/BCN = 35 : 65 : 20);
- △ sample 5 (GN/AN/BCN = 40 : 60 : 20);
- ▽ sample 6 (GN/AN/BCN = 50 : 50 : 20)

Samples 1, 2, and 3 gave lower values of n (about 0.41-0.45) than samples 5 (0.74) and 6 (0.67). For sample 4, which had a component ratio of GN/AN/BCN = 35 : 65 : 20, the value of n was 0.41 for lower pressures (between 1 and 5 MPa), while for measurements at higher pressures (between 5 and 9 MPa), the value of n was 0.77. These results suggest that the value of n for GN/AN/BCN mixtures is influenced by the pressure and GN/AN mixing ratio, and that n becomes smaller under conditions of low pressure or high AN content ; conversely, n becomes larger under conditions of high pressure or low AN content. The obtained values of a and n are shown in Table 1.

3.2 Combustion residue

Samples with smaller and greater values of n gave different residues after strand specimen combustion. For samples with smaller n , such as samples 1, 2, or 3, or 4 at lower pressure, the combustion residues took the form of a red-brown powder of copper (I) oxide (Cu_2O). In contrast, for samples with larger n , such as sample 4 at higher pressure, 5, or 6, the combustion residues were in the form of a single agglomerate of copper metal (Cu). Pictures of the combustion residues are shown in Figure 2.

3.3 Temperature profile

As described above, GN/AN/BCN mixtures can be divided into two types based on their combustion characteristics, and can be classified by component ratio, value of n , and residue type. To identify the reason for these differences, temperature profiles were obtained. Sample 4 was subjected to combustion under 1 MPa and 7 MPa of pressure to eliminate the influence of the different sample component ratios.

Figure 3 shows temperature-time curves for sample 4 under 1 MPa and 7 MPa. The horizontal line represents the distance from the combustion surface between the condensed phase and gas phase. The temperature-time curve can be divided into four zones : (1) the temperature range from room temperature to melting point (about 170°C , which is near the AN melting point of 169°C) ; (2) from melting point to about 900°C , where the pressure-independent condensed phase reaction before diffusion is predominant ; (3) from about 900°C to about 1300°C , where a pressure-dependent gas phase reaction occurs and the gases are preheated, and (4) the adiabatic combustion zone, above about 1300°C , where maximum combustion temperature is attained.

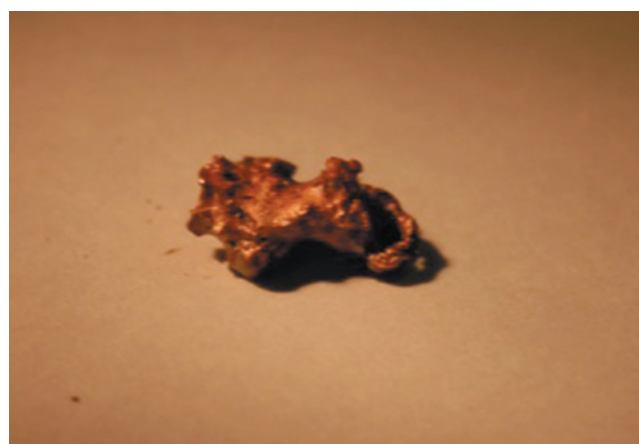
The size of the condensed phase (zone 2) was almost the same-1.2 mm-under both pressure conditions. However, one noteworthy difference was the sizes of the pre-heating zones (3) (X_{PH}). For combustion under 1 MPa, the value of X_{PH} was 3.2 mm, while for combustion under 7 MPa, the value of X_{PH} was 0.3 mm.

3.4 Discussion

Based on the results shown above, the following conclusions were drawn with regard to the combustion mechanism of the GN/AN/BCN mixture. In the solid phase in zone 1, the sample components do not start to melt or de-



(a)



(b)

Fig. 2 Combustion residues of GN/AN/BCN mixtures : (a) residue from sample 1 (GN/AN/BCN = 20:80:20, mass %) ; (b) residue from sample 5 (GN/AN/BCN = 40:60:20).

compose. The condensed phase (zone 2) is formed by melting of AN and GN, which has a melting point of 214°C . In the condensed phase, a dissociation reaction of AN into ammonia (NH_3) and nitric acid (HNO_3) is thought to take place, as indicated by Sinditskii^(6),7). HNO_3 reacts with BCN to produce $\text{Cu}(\text{NO}_3)_2$; then, up to 900°C , the diffusion of molten NH_3 and the reaction product of HNO_3 and BCN (e. g. $\text{Cu}(\text{NO}_3)_2$) into the gas-phase pre-heating zone (3) begins^(9),10). In zone 3, heterogeneous reactions between NH_3 gas and the solid reaction product of BCN, such as $\text{Cu}(\text{NO}_3)_2$ appear to take place, with the solid reaction products of BCN being reduced to Cu_2O by NH_3 ; at this stage, Cu_2O is in powdered form. Because Cu_2O has a melting point of 1232°C , the Cu_2O melts before the gas-phase substances begin adiabatic combustion above 1300°C (zone 4). The molten Cu_2O particles clump together to form aggregates. In zone 3, the diffusion rate from the condensed phase to the gas phase and the heterogeneous reactions between NH_3 and the reaction products of BCN become rate controlling ; thus, the value of n becomes smaller.

At above 1300°C , OH radicals and NO_2 -the dissociation products of HNO_3 -begin to react. In this adiabatic combustion zone, the molten aggregate of Cu_2O is reduced to metallic copper. In this zone, adiabatic combustion reactions play a dominant role ; thus, the value of n increases.

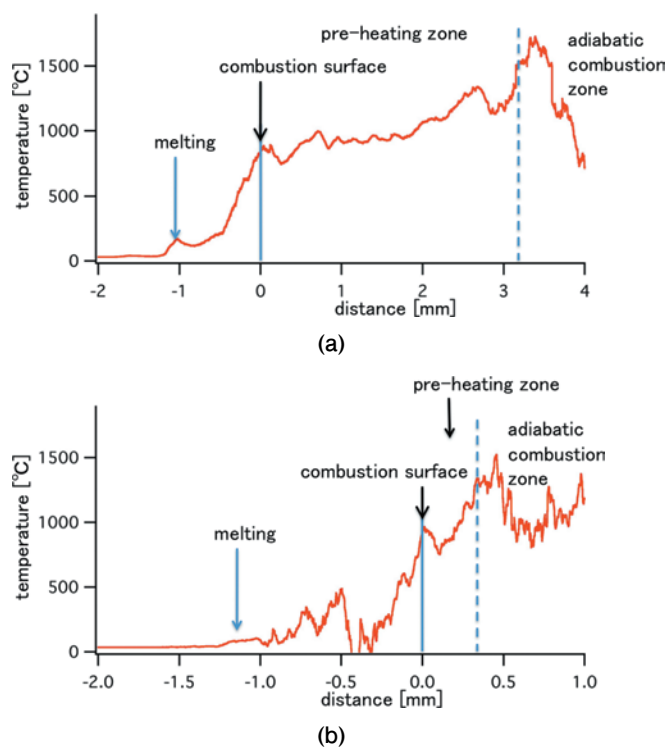


Fig. 3 Temperature profiles of sample 4: (a) temperature profile for combustion under 1 MPa pressure; (b) temperature profile for combustion under 7 MPa pressure.

Based on the experimental results and the proposed reaction mechanisms described above, the following conclusions can be drawn about the sample ratios and the value of n . The intervention of NH_3 seems to disturb the beginning of the adiabatic combustion reaction by entering a deactivation reaction with the OH radical to form an NH_2 radical and H_2O . It is suggested that for samples with a high AN content, the heterogeneous reaction between NH_3 and the reaction products of BCN become dominant, and the value of n becomes smaller, while for samples with a low AN content, the transfer into adiabatic combustion goes more smoothly, and the value of n becomes larger.

With regard to the relationship between the initial pressure and the value of n , the results of temperature profile measurements showed that the size of the pre-heating zone becomes greater under lower pressure, and thus reactions in the pre-heating zone become dominant and the value of n is smaller.

With regard to the relationship between the value of n and the residue obtained, it is suggested that as the reactions in the pre-heating zone become dominant, the amount of Cu_2O powder running off from the combustion reaction area without passing through the adiabatic combustion stage increases; thus, the residues from samples with smaller values of n contain mainly Cu_2O powder. Conversely, the residues from samples with greater values of n contain metallic copper aggregates which have passed through the adiabatic combustion stage.

4. Conclusion

The burn rates and temperature profiles of model gas

generating agents consisting of GN, AN, and BCN were measured to investigate their combustion characteristics. Based on the experimental results obtained, we engaged in some qualitative speculation about the combustion mechanism.

From the results of the burn rate measurements, it was shown that the value of the pressure exponent, n , is correlated with the sample's AN ratio and the pressure under which the experiment is conducted. The value of n becomes smaller (0.41-0.45) in samples with high AN content or under low pressure (<5 MPa) and larger (0.67-0.77) in samples with low AN content or under high pressure (>5 MPa). Temperature profile measurements clarified that the combustion wave can be divided into four zones: (1) the temperature range from room temperature to melting point (about 170°C, which is similar to the melting point of AN at 169°C); (2) from the melting point to about 900°C, where a pressure-independent condensed-phase reaction before diffusion is predominant; (3) between about 900°C and about 1300°C, where a pressure-dependent gas phase reaction occurs and the gases are preheated; and (4) the adiabatic combustion zone above about 1300°C, where the maximum combustion temperature is attained. Based on these results, it was suggested that the value of n is affected by the sample's AN content and the pressure under which the test is conducted, due to the influence of the pre-heating zone reaction.

Acknowledgements

This work was supported in part by the Global COE Program "Chemistry Innovation through Cooperation of Science and Engineering", MEXT, Japan.

References

- 1) U.S. Patent 20030057398
- 2) N. I. Golonova, G. N. Nechiporenko, G. G. Nemtsev, G. P. Dolganova, V. P. Roshchupkin, D. B. Lempert, G. B. Manelis, *Russ. J. Appl. Chem.*, 80, 24 (2007)
- 3) I. V. Khoruzhii, G. F. Klyakin, V. A. Taranushich, V. I. Lachin, *Russ. J. Appl. Chem.*, 81, 61 (2008)
- 4) G. B. Manelis, G. M. Nazin, Yu. I. Rubtsov, V. A. Strunin, "Thermal Decomposition and Combustion of Explosives and Propellants", (2003) Taylor & Francis
- 5) K. R. Brower, J. C. Oxley, M. Tewari, *J. Phys. Chem.*, 93, 4029 (1989)
- 6) V. P. Sinditskii, V. Yu. Egorshv, A. I. Levshenkov, V. V. Serushkin, *Propellants, Explosives, Pyrotechnics*, 30, 269 (2005)
- 7) K. K. Kuo, K. Hori, "Advancements in Energetic Materials and Chemical Propulsion", (2008) Begell House, Inc.
- 8) M. Ichino, T. Yokoyama, S. Oda, Y. Iwai, *Nippon Kagaku Kaishi*, 2002, 281 (2002)
- 9) R. J. Doyle, Jr., *J. Am. Chem. Soc.*, 116, 3005 (1994)
- 10) Ph. Otten, F. Bruynseels, R. Van Grieken, *Anal. Chim. Acta*, 195, 117 (1987)

硝酸グアニジン，硝酸アンモニウム， 塩基性硝酸銅混合物の燃焼機構

和田祐典^{*†}，堀恵一^{**}，新井充^{***}

自動車用エアバッグガス発生剤の新規酸化剤候補として硝酸アンモニウム（以下，ANと略記）の実用化を目指し，硝酸グアニジン（以下GNと略記），塩基性硝酸銅（以下，BCNと略記），ANからなるモデルガス発生剤の燃焼挙動が検討された。ストランド燃焼試験の結果より，以下の結論が示された。(1)BCNの添加がGN/AN混合物の着火を実現し，低圧条件下（約1 MPa）における持続燃焼を実現すること。(2)GN/AN/BCN混合物の燃焼残渣の様子が燃焼条件と試料の混合組成によって異なる事。(3)圧力指数は高AN含有量または低圧下（5 MPa以下）では0.41から0.45となり，一方で低AN含有量または高圧下（5 MPa以上）では0.67から0.77となること(4)燃焼波は温度と相状態から4つの領域に分けられること。以上の結果から，拡散燃焼と均質燃焼が共存する燃焼機構モデルが提案された。

* 東京大学大学院工学系研究科化学システム工学専攻 〒113-8656 東京都文京区本郷7-3-1
TEL 03-5841-2980

†Corresponding address : yusuke.wada@aist.go.jp

** 独立行政法人宇宙航空研究開発機構宇宙科学研究本部 〒229-8510 神奈川県相模原市由野台3-1-1

*** 東京大学環境安全研究センター 〒113-0033 東京都文京区本郷7-3-1