Research paper

Investigation on the properties of a high nitrogen compound

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Abstract

A high nitrogen compound, guanylaminotetrazole (GAT), has been investigated as a possible fuel component for gas generant. The thermal behaviors of GAT were evaluated by DTA-TG tests. In high temperature deterioration test, the lost weight of the material was only 0.2 % when heated for 400 hrs at 383 K, and neither discoloration nor deterioration in appearance was observed. In addition, GAT was found to be insensitive to impact and friction. The combustion properties of a stoichiometrically mixed GAT / Sr $(NO_3)_2$ were investigated. The results indicated that the mixture demonstrated excellent combustion properties and generation of sufficient gas to use inflate airbag.

Keywords: High nitrogen compound, Guanylaminotetrazole, Tetrazole, Gas generant

1. Introduction

In order to protect drivers and passengers from traffic accidents, recently, most of automobiles are equipped with airbag systems. Gas generants for inflating automobile airbag are most commonly based on sodium azide, which produces nitrogen gas. However, due to toxicity problems of sodium azide, which poses a problem for handling in the manufacture, storage and eventual disposal of un-deployed units, a number of non-azide gas generant ingredients have been proposed to substitute sodium azide. On the other hand, non-azide compounds tend to present their own problems, such as thermal stability, ignition and combustion performance.

The derivatives of five-number high nitrogen-containing heterocycles (tetrazole) and various guanidines are of interest for use as stable energetic compounds, such as gas generant. A high nitrogen compound, guanylaminotetrazole (GAT) is a unique compound composed of guanyl fragment with tetrazole cycle in one molecule, which would possess positive properties of both groups, thus combining high nitrogen content and thermal stability with low sensitivity to impact and friction. In this work, the properties of GAT were investigated in order to learning the thermal stability, ignitability, sensitivity to impact and friction, and combustion properties of the material. In addition, the properties of GAT were compared with that of 5-aminotetrazole (5-ATZ), because 5-ATZ has been extensively studied and utilized as a fuel component for gas generants.

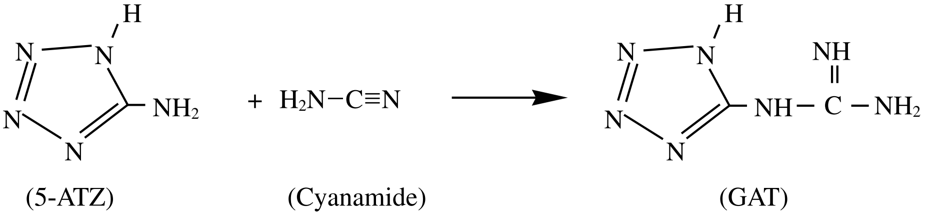

Fig. 1 Synthesis of GAT.

2. Synthesis of GAT

The synthesis of GAT was described in detail by S. Helf, *et al.*[1] and only a brief overview will be given here. 5-ATZ was added to the cyanamide solution that was neutralized to a pH of 7 with dilute ammonium hydroxide and the mixture was immersed in a steam bath and heated with stirring. 5-ATZ went into the solution after 30 minutes and upon continued heating and concentration of the mixture, GAT began to precipitate. The reaction can be represented by the formula shown in Fig. 1.

3. Experimental

3.1 Thermal stability test

Differential thermal analysis (DTA) and thermogravimetry (TG) were carried out using SEIKO TG / DTA320 apparatus for evaluating the thermal behaviors of GAT. The test was performed with 5 mg sample contained in alumina crucibles under nitrogen atmosphere. The applied heating rate was 10 K·min^{-1}.

In high temperature deterioration test, the testing samples were subjected to 383 K for 400 hours.

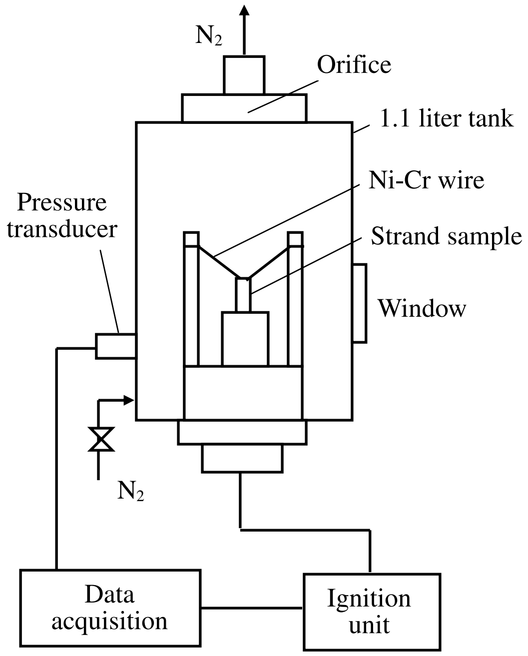

Fig. 2 Experimental setup for chimney-type strand burner.

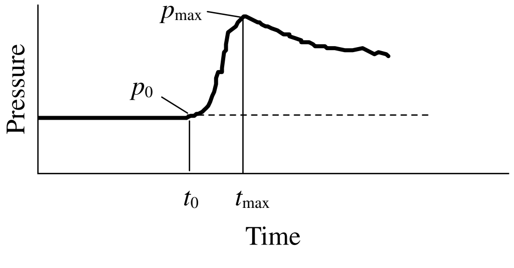

Fig. 3 Typical pressure profile in chimney-type strand burner. (burning time = t_{max}- t_0)

3.2 Sensitivity test

Impact sensitivity test and BAM friction sensitivity test were conducted according to Japanese Explosive Standard ES-21 and ES-22, respectively.

3.3 Ignitability test

The sample of GAT used to determine the ignitability was piled on an adiabatic plate in the open air. A quick match was applied to ignite the sample. The weight of the sample was 3 grams. In the same way, a hot Ni - Cr wire was applied to ignite the sample until it ignited or for a maximum of 2 minutes.

3.4 Burning rate measurement

The burning rate of GAT / oxidizer mixture was measured with a chimney-type strand burner pressurized with nitrogen gas. Strontium nitrate (Sr $(NO_3)_2$) was used as an oxidizer. The weight ratio of GAT and Sr $(NO_3)_2$ was 0.46, which was nearly stoichiometric. The sample was pressed into a strand 6 mm × 6 mm in cross section by 30 mm in length at approximately 300 kgf and was then coated on the sides with an epoxy resin inhibitor which prevented burning along the sides. Figure 2 is a schematic diagram of the experimental setup. The pressure inside the strand burner was measured with a pressure transducer. The output of the pressure transducer was transferred to a data acquisition system. Figure 3 shows an example of a typical pressure profile. The pressure started to rise when the strand was ignited at its end and the pressure reached a maximum when the flame propagated to the other end of the strand so that the time between t_0 and t_{max} in Fig. 3 was the burning time that could be measured from the pressure profile. The burning rate was determined by the length of the strand and the burning time. The tests were conducted in the ambient pressure of 1 - 8 MPa.

3.5 60 liter tank test

The combustion properties of GAT / Sr $(NO_3)_2$ mixture were investigated with 60 liter tank test. GAT / Sr $(NO_3)_2$ mixture in a weight ratio of 0.46 was wet blended and was granulated by passing through a sieve. The granulated mixture was dried in an oven and then was pressed into pellets having 6 mm diameter by 3 mm thickness. The pellets of 30 g were loaded into a combustion chamber shown in Fig.

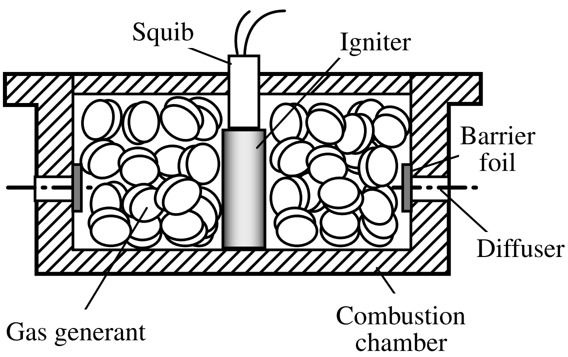

Fig. 4 Schematic diagram of combustion chamber.

4, which was similar to an inflator. The combustion chamber equipped with a conventional 1.5 g B / KNO_3 igniter. The diffusers on the combustion chamber were sealed with aluminum barrier foil, which allowed the pressure to build up in the combustion chamber before the foil burst-out. The combustion chamber was mounted inside a 60 liter tank. Figure 5 is the schematic diagram of the 60 liter tank test system. The pressure profiles in the combustion chamber and in the tank were recorded by a data acquisition system.

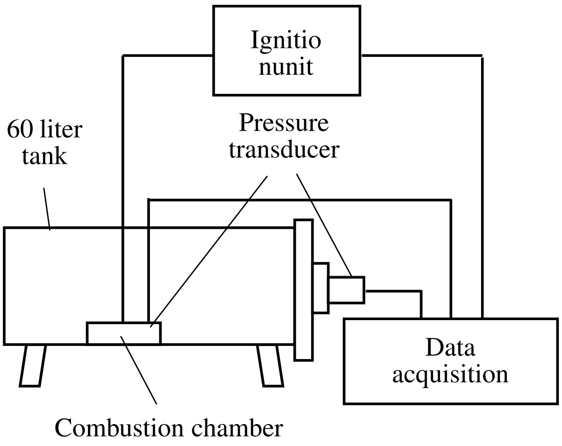

Fig. 5 Experimental setup for 60 liter tank test.

4. Results and discussion

4.1 Physical and thermochemical properties

The physical and thermochemical properties for both GAT and 5-ATZ from literatures[1), 2), 3)] are shown in Table 1.

Table 1 Physical and thermochemical properties.

	GAT	5-ATZ
Molecular weight (kg·mol^{-1})	127.1×10^{-3}	85.68×10^{-3}
Density (kg·m^{-3})	1.41×10^{3}	1.50×10^{3}
Melting point (K)	>573	482 - 483
Enthalpy of formation (kJ·mol^{-1})	135.56	207.78

The theoretical adiabatic combustion temperatures for GAT / Sr $(NO_3)_2$ and 5-ATZ / Sr $(NO_3)_2$ are 2457 K and 2682 K, respectively. The combustion temperature of GAT / Sr $(NO_3)_2$ is lower than that of 5-ATZ / Sr $(NO_3)_2$. Therefore, GAT is a preferred fuel component due to its low combustion temperature.

4.2 Thermal stability

Two kinds of GAT samples were investigated by DTA-TG tests. One was pure GAT, which was improved by dilution of the mother liquor with water and further concentration on the steam bath. Another was impure GAT, which was not further improved so that it contained some 5-ATZ.

Typical DTA-TG curves of pure GAT and impure GAT are shown in Fig. 6 and Fig. 7, respectively. The DTA curve in Fig. 6 shows that the pure GAT does not melt up to a temperature of 583 K, i.e. it is thermal stable below 583 K. On the contrary, the DTA curve of 5-ATZ reported by Miyako Akiyoshi *et al.*[4)] shows that 5-ATZ starts to melt at a lower temperature of 473 K and soon an exothermal decomposition occurs over a wide temperature range.

The DTA and TG plots of impure GAT in Fig. 7 show two endothermic peaks of which the first one is mainly due to the melting of 5-ATZ at a temperature of 468K and the second one is mainly due to the melting of GAT at 583 K. After the first endothermic peak, it soon starts to decompose exothermally and the lost weight is about 21 %, which is similar to the thermal behavior of 5-ATZ. Therefore, the thermal stability of the pure GAT is better than that of GAT containing some 5-ATZ.

Figure 8 displays the results of high temperature deterioration test. The lost weight of pure GAT is only 0.2 % when heated for 400 hrs at 383 K, and there is neither discoloration nor deterioration in appearance, which indicates that the pure GAT is an excellent thermally stable material.

4.3 Sensitivity to impact and friction

In impact sensitivity test, GAT did not detonate when a 5 kg drop hammer fell onto the material from 0.5 m height. In BAM friction sensitivity test, GAT did not explode with the load of 353 N. According to Japan Explosive Society Standard, the impact sensitivity and fiction sensitivity of GAT can be classified into grade 8 and grade 7, respective-

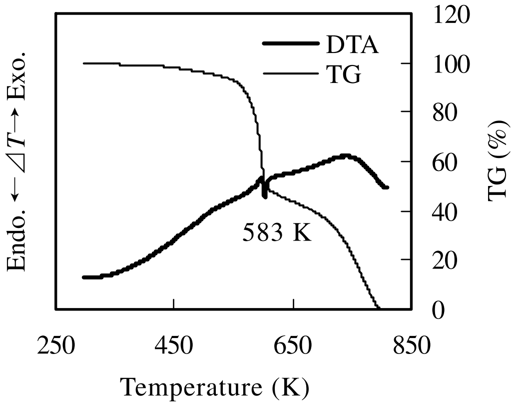

Fig. 6 DTA-TG plots for pure GAT.

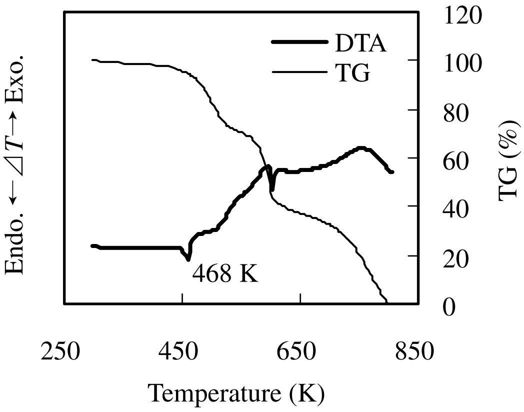

Fig. 7 DTA-TG plots for impure GAT.

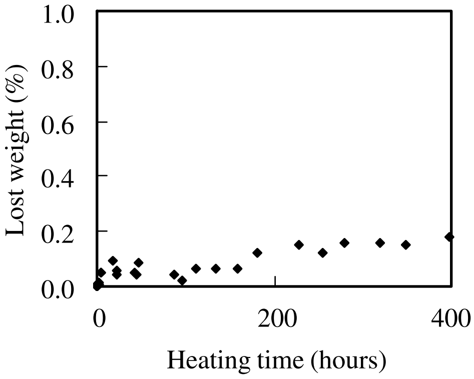

Fig. 8 Lost weight of pure GAT heated at 383 K.

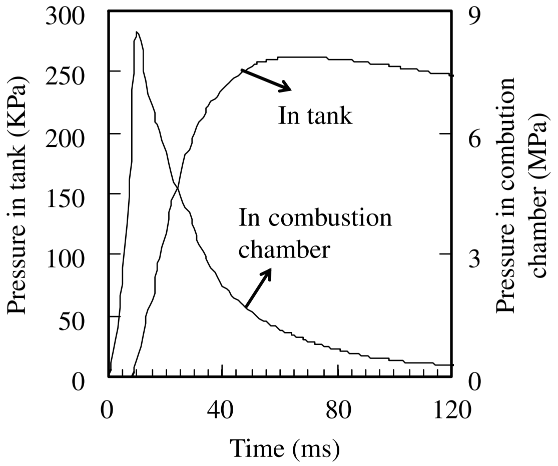

Fig. 9 Typical pressure profiles in combustion chamber and in 60 liter tank for GAT / Sr $(NO_3)_2$.

ly. The larger the number of grade is, the less the sensitivity is. It is reported[5)] that the impact sensitivity and friction sensitivity of 5-ATZ are classified into grade 8 and grade 7, respectively. GAT appears considerably insensitive to impact and friction as well as 5-ATZ. Therefore, the material is safe for handling as a pyrotechnic material.

4.4 Ignitability

In ignitability tests, GAT sample was ignited in the open air by a quick match or a hot wire. Once ignited, GAT sample burns continuously. The results indicate that the GAT tested in this study is an ignitable and combustible material for practical applications.

4.5 Burning rate

The burning rate under pressurized condition for GAT / Sr $(NO_3)_2$ can be expressed by the following Vieille equation:

$$r = ap^n \tag{1}$$

where p is the ambient pressure, n is the pressure exponent and a is a constant. The measurement results of burning rate are showed in Table 2. The data of 5-ATZ / Sr $(NO_3)_2$ reported by Yasuyoshi Miyata *et al.*[6)] are also listed in the Table 2.

As shown in Table 2, the burning rate of GAT / Sr $(NO_3)_2$ is larger than that of 5-ATZ / Sr $(NO_3)_2$. The pressure exponent of GAT / Sr $(NO_3)_2$ is low and is acceptable for the purpose of practical application. A relatively low pressure exponent, such as between zero and 0.6 is preferable in the case of airbag because the lower the pressure exponent is, the less the influence of the pressure on the burning rate is. If pressure exponent is high, it is difficult to control the burning rate or pressure inflating airbag.

Table 2 Burning rate.

	GAT / Sr $(NO_3)_2$	5-ATZ / Sr $(NO_3)_2$
r (at 2MPa)	8.63 $(mm \cdot s^{-1})$	7.59 $(mm \cdot s^{-1})$
a	2.11	—
n	0.47	—

4.6 Pressure in 60 liter tank

Typical pressure profiles in the combustion chamber and in the 60 liter tank during the reaction are illustrated in Fig. 9, respectively. This measurement was designed to predict the pressure profile, which would be experienced in the actual airbag. It is required that the pressure should build up in a short period of time. Therefore, the onset time of pressure rise and the rate of pressure rise in the tank are the important parameters for evaluating the combustion properties of gas generants.

After ignition, the generated gas was stored and pressure built up in the combustion chamber. The stored gas was released into 60 liter tank when the foil burst. The pressure profiles in Fig. 9 show that the onset time of pressure rise in the tank is less than 10 ms. The average rate of pressure rise during 50 ms after the onset of pressure rise in 60 liter tank for GAT / Sr $(NO_3)_2$ gas generant is 170 $MPa \cdot s^{-1} \cdot kg^{-1}$. It is reported[7)] that the average rate of pressure rise during 50 ms after the onset of pressure rise in 60 liter tank for 5-ATZ / Sr $(NO_3)_2$ is about 150 - 160 $MPa \cdot s^{-1} \cdot kg^{-1}$. The results indicate that the burning rate of GAT / Sr $(NO_3)_2$ is larger than that of 5-ATZ / Sr $(NO_3)_2$ which has already been used in practical application[4)]. Therefore, GAT / Sr $(NO_3)_2$ mixture has good ignition and combustion characteristics, and can produce sufficient gas to inflate airbag in a short time.

In addition, the following test was also conducted for evaluating the influence of environmental temperature. The temperature of combustion chamber was kept constant at the required temperature (353 K and 296 K) for a minimum of 4 hours. Then, the combustion chamber was mounted in the test tank and the gas generant was ignited. Figure 10 displays the typical pressure profiles in 60 liter

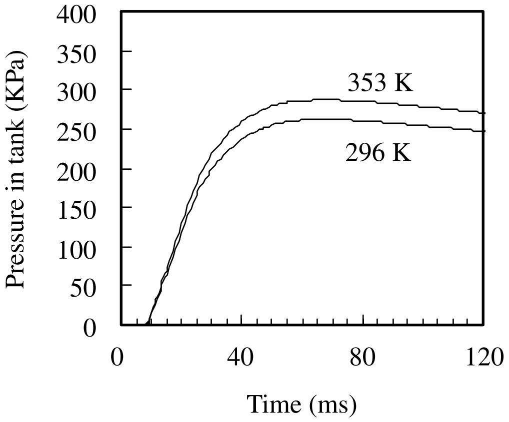

Fig. 10 Typical pressure profiles in 60 liter tank for GAT / Sr $(NO_3)_2$ at 353 K and 296 K, respectively.

tank at the temperature of 353 K and 296 K, respectively. The difference of the maximum pressure between 353 K and 296 K did not exceed 25 KPa. The result suggests that the combustion performance of GAT / Sr $(NO_3)_2$ mixture is less affected by an environmental temperature.

5. Conclusions

The properties of a high nitrogen compound, GAT, have been evaluated by the thermal stability test, sensitivity test, ignitability test and combustion tests in this work. GAT has been found to be a preferable fuel component utilized in gas generant for its excellent thermal stability, which insures the reliability of the gas generant over long periods. GAT is insensitive to impact and fiction, so that the material is considered safe for handling in manufacturing processes. In addition, in view of its excellent combustion properties, GAT / oxidizer mixture is acceptable as a component of gas generant.

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