Research paper

The mixture of the phase stabilized ammonium nitrate containing potassium nitrate and 1HT as the new gas generant composition

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Abstract

  A new gas generant for air bags was investigated. Ammonium nitrate (AN) does not give off harmful gases or solid burning residues but goes through contraction and expansion during a series of phase transitions which cause structural damage. In this study, potassium nitrate–phase stabilized ammonium nitrate (PSANKN) was prepared by a nonhazardous aqueous method. Thermal analysis indicated that PSANKN without the phase transition near room temperature was obtained by adding more than 5 wt% potassium nitrate. 1H-tetrazole (1HT) was selected because it has a large heat of formation and decomposes by itself in N_2 atmosphere and the burning of 1HT/AN mixture has been reported. The melting point, burning rate, gas generation ability by means of 4 L tank test, the mol% and wt% of each generated product, efficiency of gas evolution, wt% of solid products, number of moles of generated gas per 100 g of gas generant, wt% of solid products, calorific value of per mole of gas generates, and sensitivities were obtained to evaluate the characteristics that indicate desirable gas generants.

Keywords : PSAN, 1H-tetrazole, gas generant, burning rate, 4 L tank test

1. Introduction

  An air bag is a vehicle safety device and designed to inflate rapidly during an automobile collision. Its purpose is to cushion occupants during a crash and provide protection to their bodies. After the onset of the crash, the signals from the impact sensors are fed into the air bag control unit which will trigger the ignition of a gas generant to rapidly inflate a fabric bag in 25 – 50 ms. Once an air bag deploys, deflation begins in 80 – 100 ms as the gas escapes through vents in the fabric. Deployment is frequently accompanied by the release of dust-like particles, and gases in the vehicle's interior.

  The desirable performances of the gas generant for air bags are as follows[1].

  (1) For gas generants to be useful in automotive applications, they must be thermally stable when aged for 400 h or more at 380 K. The compositions must also retain structural integrity when cycled between 233 and 380 K.

Any phase stabilized ammonium nitrate (PSAN)–nonazide fuel mixture with a melting point of less than 388 K will decompose when aged at 380 K[2]. Therefore it is desirable that the melting point of the gas generant is higher than 388 K.

  (2) Basic burning characteristics of gas generant are evaluated by means of a chimney-type strand burner and a 60 L tank. Gas generant generally require a burning rate of at least 10 mm·s^{-1} or more at 7 MPa, because composition with a burning rate less than this do not ignite reliably and often result in "no–fires" in the inflator[2]. Burning rates of energetic materials generally follow Vieille's law, given by $r = a \cdot P^n$, where a is a constant that depends on the chemical composition and initial propellant temperature, and n is the pressure exponent of the burning rate[3]. The pressure exponent should be as close to zero as possible. As n increases, a very small change in pressure will result in a large change in the burning rate,

which could result in high performance or ballistic variability, or over–pressurization. Therefore, for automotive air bag applications, n of approximately 0.30 or less is desirable over the operating pressure of the inflator[4] or 0.5 for mass burning rate[5].

(3) It is preferable that the gas generants produce no harmful gasses, because air bag release the combustion gases inside a vehicle after its deployment to maintain the driver's view[1].

(4) It is desirable that the gaseous products are more than 90 % of the total product mass, and that solid products are 10 % or less of the total product mass[2]. The number of moles of generated gas is adjusted more than 2.70 mol per 100 g of gas generant[6]. The primary gaseous products for carbon atoms and nitrogen atoms in the gas generants are CO_2 and N_2, respectively. H_2O, when produced, is also considered as a gas in the calculation of these values because it is usually fed to the air bag in the form of a gas[6]. When produced H_2O content increases, the deployment temperature and the quantity of steam decrease and the pressure in the air bag tends to fall down. Therefore, it is preferable mol% of H_2O is lower than 50 %[7].

(5) The temperature of the generated gas must be designed to the lowest possible temperature to reduce damage to the air bag and eliminate burn injury of a vehicle occupant. It is preferable that the calorific value per gram of gas generant composition is not more than 4500 J[6] and the adiabatic flame temperature (T_f) of the gas generant is 2273 K or less[8]. It is a very important factor to realize reduction in the size and weight of the gas generator to suppress the calorific value per mole of gas generated by the combustion of the gas generant. The gas generator using gas generant that generates a large calorific value requires a large amount of coolants, so that it is hard to realize reduction in size and weight of the gas generator. If the temperature of the generated gas is too low, a large number of moles of gas generated, i.e., a large amount of gas generant, will be needed for obtaining a required gas volume for inflating the air bag. It is most preferable for the gas generant to realize a reduction in the size and weight of the gas generator, so that the calorific value per mole of generated gas is set to be in the range of 95 to 105 kJ.

(6) It is necessary to avoid material that may cause detonation or spontaneous combustion during the manufacturing process[1].

Ammonium nitrate (AN) has attracted attention over the years as an oxidizer for environmentally friendly, clean gas generating compounds because it does not give off harmful gases or solid burning residues, advantages that generally fulfill the strict requirements imposed on gas generants for vehicle air bag systems. Besides, AN is one of the cheapest and easily available compounds. However, AN has its disadvantages in that it is hygroscopic, which becomes a problem during manufacture and storage, and AN undergoes contraction and expansion during a series of phase transitions. AN shows several phase transitions such as AN$_V$ (tetragonal)⇄AN$_{IV}$ (rhombic tripyramidal)⇄

AN$_{III}$ (orthorhombic)⇄AN$_{II}$ (tetragonal)⇄AN$_I$ (cubic) at 256, 305, 357, and 398 K, respectively[9]. The phase transformation around room temperature results in crack formation in the propellant grain. The phase stabilization of AN has been achieved using additives such as potassium nitrate (KN)[9]−[12], CuO[9],[13],[14], KF[9],[15], and various organic compounds[16].

In this study, PSAN was prepared by a nonhazardous aqueous method for a new gas generant. The composition of the solid crystallized from AN–KN solution at approximately 363 K was reported to be almost the same as that of the solution[11] ; therefore, AN–KN solutions were evaporated to dryness at 363 K and then ground to obtain potassium nitrate–phase stabilized ammonium nitrate (PSANKN).

However, there is a problem in that AN alone is difficult to burn, i.e., AN has poor thermal and combustion reactivity, so that AN-based gas generants prepared by mixing with organic fuels have low burning rates. We have previously investigated gas generants that utilize AN and energetic tetrazoles such as aminoguanidinium 5,5'-azobis-1H-tetrazolate (AGAT)[17],[18] and 1H-tetrazole (1 HT)[19]. AGAT, which decomposes by itself at approximately 1 mm·s^{-1} in a 1 MPa N_2 atmosphere has been examined as a fuel to mix with AN[20]. 1HT has a large heat of formation (301.62 kJ·mol^{-1} [21]) and preliminary experiments revealed that 1HT also decomposes by itself at 5.52 mm·s^{-1} in a 1.1 MPa N_2 atmosphere, which suggests that 1HT can be used as a fuel with AN as an oxidizer. In this study, a mixture of 1HT and PSANKN was investigated.

2. Experimental
2.1 Materials

To obtain PSANKN, the designated weight of AN and KN were dissolved in a small amount of water. The solution was then heated to dissolve the chemicals and the solution was kept at 363 K in a thermostatic oven until completely dry. Dried PSANKN was milled with a vibration ball mill, followed by sieving through JIS Z8801 sieves. In this study, PSANKNX denotes AN containing X wt% KN. 1HT (Toyo Kasei Kogyo Co. Ltd.) was also dried in vacuum and sieved. Figure 1 shows the chemical structure of 1HT. The particle sizes of PSANKN and 1HT were in the range of 75-150 μm. 1HT and PSANKN5 were mixed at a ratio of 23.43 : 76.57 (w/w). For the 4L tank test guanidine nitrate (GN), strontium nitrate (SrN), copper nitrate basic (BCN) were mixed in a ratio of 56.05 : 19.45 : 24.50 (w/w). Fuel particles and oxidizer particles were mixed for 30 min at 80 rpm using a rotary mixer.

2.2 Thermal analysis

Thermogravimetry (TG) and Differential thermal analysis (DTA) were conducted at the heating rate of 5 K· min^{-1} in a He atmosphere (flow rate 20 mL·min^{-1}) using an aluminum cell (DTG-50H, Shimadzu Corp.). Melting point was determined using a capillary method melting point apparatus at a heating rate of 10 K·min^{-1} and by differential scanning calorimetry (DSC ; DSC-50,
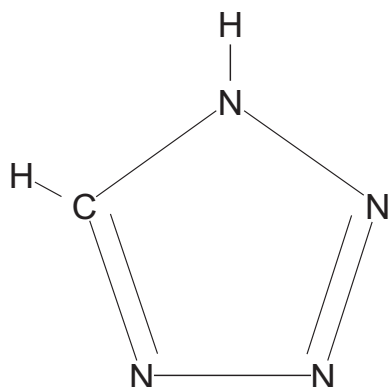
Figure 1　Chemical structure of 1H−tetrazol.

Shimadzu Corp.) at a heating rate of 5K·min^{-1} in a N_2 atmosphere (flow rate 20mL·min^{-1})using an aluminum cell.

2.3 Burning rate

The method used to determine the burning rate has been reported elsewhere[19]. A 1.5-g quantity of the stoichiometric 1HT/PSANKN5 (23.43 : 76.57) mixture was uniaxially pressed at approximately 300 MPa for 3 min to form cylindrical pellets (diameter 10 mm, thickness 11 mm). The side of the cylindrical pellet was coated with epoxy resin to ensure cigarette burning. Combustion tests were performed using a pressure and temperature controlled chimney-type strand burner with an optical window (TDK-15011, Tohata Denshi Co. Ltd.), under a N_2 atmosphere in the range of 1-10 MPa. The initial temperature was set to 296 K. Ignition of the pellet was carried out with a electrically heated nichrome wire (diameter 0.6 mm) by means of a regulated DC power supply. The pressure in the chamber was measured with a pressure sensor and after amplification through a signal amplifier, the data were recorded using a digital data recorder. From the acquired pressure-time data, as shown schematically in Figure 2, the burning rates (r) were deduced from the duration of the recorded pressure increase. The pressure began to increase as soon as the sample started to burn and stopped increasing when combustion ceased. The average internal pressure (P) was calculated by averaging the pressures at the start and end of burning.
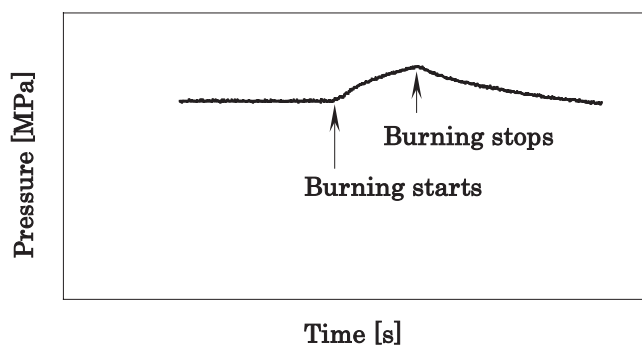

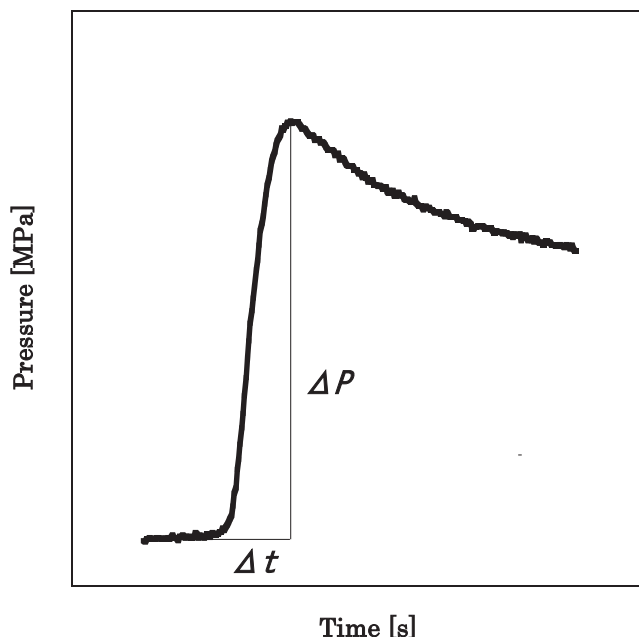Figure 2　Schematic diagram of pressure−time history from burning rate measurement.

Figure 3　Schematic diagram of 4 L tank test.

2.4 Four L tank test

Gas generation ability, which is generally measured by a 60 L tank test, was investigated using a 4 L tank test (or closed vessel test) in this study. A 4-g quantity of dried mixture was uniaxially pressed at approximately 200 MPa for 3 min to form cylindrical pellets (diameter 14.7 mm, thickness 13.5-14.5 mm). The pellet was uniformly coated with epoxy resin to achieve cigarette burning. A 4 L chimney-type strand burner (SCTA-50, Kyowa Giken Co., Ltd.)[22], which had been used for the measurement of the burning rate and no modification was undertaken other than closing the exit of gas flow, was used as the burning test apparatus. The 4 L tank tests were conducted at an initial temperature of 296 K and an initial pressure of 2 MPa. Ignition of the top surface of the sample was achieved using an electrically heated nichrome wire. The internal pressure of the vessel was monitored using a pressure transducer, and after signal amplification through a signal conditioner, the signal was recorded on a digital data recorder. From the acquired pressure-time data, as shown schematically in Figure 3, the net pressure increase (ΔP), which is the difference between the initial pressure and maximum pressure, and Δt, which is the time duration from the onset of pressure increase to the time when the pressure reaches the maximum pressure, were calculated to determine the rate of pressure increase ($\Delta P/\Delta t$).

2.5 Chemical equilibrium calculation

Chemical equilibrium calculation was conducted using ICT-Thermodynamic code[23].

2.6 Sensitivity

In order to investigate the sensitivity of tetrazoles, drop hammer and friction tests were conducted according to the regulations of the Japan Explosives Society[24].

3. Results and discussion
3.1 Thermal analysis

The prepared PSANKN samples were compared with pure AN to determine if the undesirable phase changes near room temperature had been eliminated. Figure 4 shows DTA curves of AN, KN, and PSANKN. Endothermic peaks of pure AN at 307, 359, and 401 K indicate $AN_{IV} \rightleftarrows AN_{III} \rightleftarrows AN_{II} \rightleftarrows AN_{I}$ phase transitions, respectively and that at 443 K corresponds to the melting of PSANKN. Increase in the KN content resulted in an increase of the $AN_{IV} \rightleftarrows AN_{III}$ phase transition temperature and the endothermic peak disappeared at 5 wt% KN, which indicates PSANKN without the $AN_{IV} \rightleftarrows AN_{III}$ phase transition near room temperature can be obtained by adding more than 5 wt% KN. It is desirable to produce less

solid products so that the minimum amount of KN was used to stabilize AN.

The weight fraction of KN in the precipitate was determined by TG[10]. The weight percentage of remnants from PSANKN 1, PSANKN 2, PSANKN 3, PSANKN 4, PSANKN5, PSANKN10, and PSANKN15 were 1.0, 2.0, 2.9, 3.9, 4.8, 9.1, and 13.1 %, which are in relatively good agreement with the weight percentage of KN in PSANKN. This supports the report that the composition of PSANKN crystallized from AN-KN solution at approximately 363 K is almost the same as that of the solution[10].

The melting point of 1HT/PSANKN5 was 374-391 K, which was lower than the desirable 388 K[2]. The melting point determined by DSC was 372 K. The addition of SrN and clay would help to improve the melting point[25] and
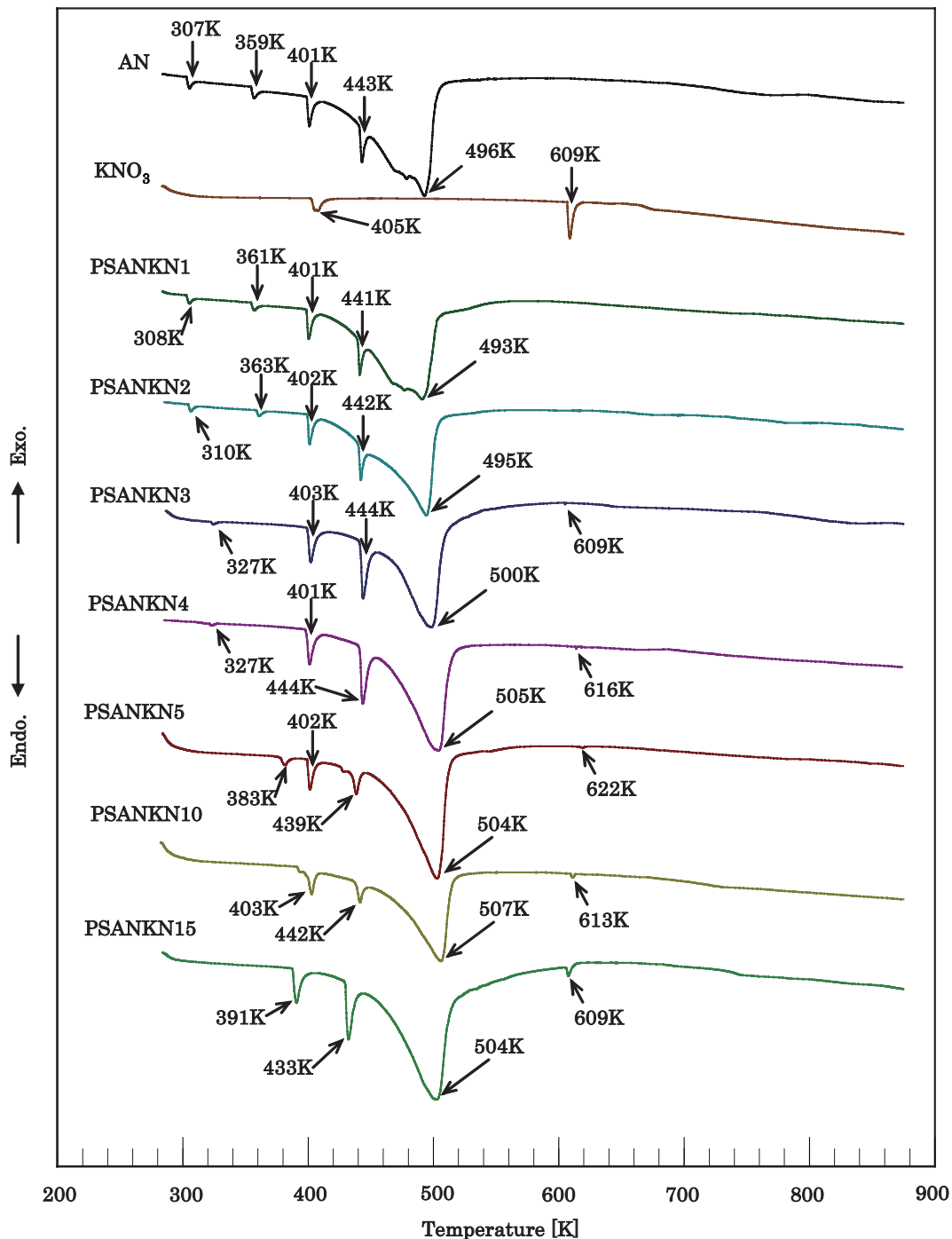
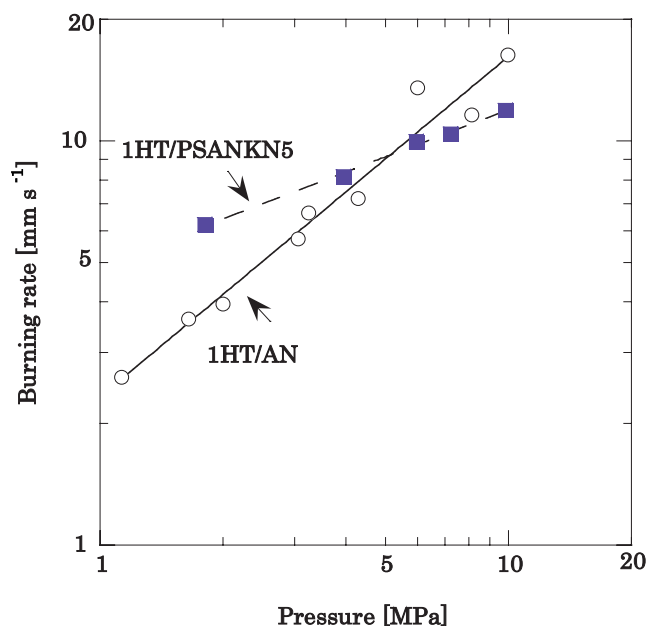**Figure 4**   DTA curve of AN, KN, and PSANKN.

Figure 5   Burning rate for 1HT/PSANKN5 and 1HT/AN.

Figure 6   Pressure−time histories of mixtures from 4 L tank test.

3.2 Burning rate

The results of the burning rate tests for the 1HT/PSANKN5 and 1HT/AN mixtures are presented in Figure 5 for 296 K. The burning rates of the samples were confirmed to follow Vieille's law.

At 2 MPa the burning rate of 1HT/PSANKN5 was approximately 1.5 times as high as that of 1HT/AN, although the difference decreased as the pressure increased, and at 5 MPa the burning rate of 1HT/AN exceeded that of 1HT/PSANKN5. The values of a and n for 1HT/PSANKN5 were determined to be 4.91 and 0.385, respectively, and the burning rate at 7 MPa was 10.4 mm·s^{-1}, which is slightly higher than the desirable 10 mm·s^{-1} [2]. The pressure exponent n is larger than the preferable value of 0.3 [4].

3.3 Four L tank test

The results for the 4 L tank tests are shown in Figure 6 and Table 1. Each sample was ignited and burnt completely. The rate of gas generation ($\Delta P/\Delta t$) for the 1 HT/PSANKN5 was 0.232 MPa·s^{-1}, which was approximately 1.4 times that for the GN/SrN/BCN mixture (0.164 MPa·s^{-1}) and 0.49 times that for the 5-ATZ/SrN mixture (0.487 MPa·s^{-1}), which are two examples of gas generants used in practical applications. The rate of gas generation was almost the same as that for GN/SrN/BCN up to 3 s, and faster than that afterward.

3.4 Chemical equilibrium calculation

Chemical equilibrium calculations [23] were conducted to obtain the mol% and wt% of each generated product, the total amount of generated gases, heat of explosion, and T_f, and the results are presented in Table 2.

It was found that generated gaseous products were harmless CO_2, H_2O, and N_2. The molar percentage of H_2O was slightly higher than the acceptable value of 50 [7], which

Table 1   Gas generation ability for the mixtures.

Mixtures	Initial pressure [MPa]	Maximam pressure [MPa]	ΔP [MPa]	Elapsed time [Δt] [s]	Rate of gas generation [$\Delta P/\Delta t$] [MPa s^{-1}]
1HT/PSANKN5	2.049	3.048	0.999	4.30	0.232
1HT/AN	2.038	2.846	0.808	7.42	0.109
5-ATZ/SrN	2.043	2.866	0.823	1.72	0.478
GN/SrN/BCN	2.046	2.717	0.671	4.10	0.164

SrN : Strontium nitrate, GN : Guanidine nitrate, BCN : Copper nitrate basic

Table 2   Results of chemical equilibrium calculation for 1HT/PSANKN5.

		[mol%]	[wt%]
Generated products	CO_2	7.738	13.908
	H_2O [l]	52.684	38.759
	N_2	39.098	44.726
	KOH [s]	0.024	0.056
	K_2CO_3[s]	0.451	2.547
Total amount of generated gases	[mol·kg^{-1}]	40.642	
Heat of explosion [water gaseous]	[J·g^{-1}]	4134.7	
Adiabatic flame temperature	[K]	3035.3	

[s] : solid, [l] : liquid

could be improved by replacing AN with other oxidizers that produce less water. The calorific value per gram of gas generant was 4134.7 J·g^{-1} which was lower than the desirable 4500 J·g^{-1}. T_f was 3053 K which was higher than the desirable 2273 K.

Based on the results in Table 2, the following results were obtained. The efficiency of gas evolution was 97.4 % which was higher than the desirable 90 %. The wt% of solid products was 2.6 % which was less than the desirable 10 %. The number of moles of generated gas per 100 g of

gas generant was 4.06 mol·$(100 \text{ g})^{-1}$ which was higher than the desirable 2.70 mol·$(100 \text{ g})^{-1}$. The calorific value per mole of generated gas was 101.7 J·mol^{-1} which was in the range of desirable 95 - 105 J·mol^{-1}. It was found that the calculated results of 1HT/PSANKN5 were acceptable values for a practical gas generant.

3.5 Sensitivity

1HT/PSANKN5 did not ignite even at a drop height of 50 cm (highest point of 1/6 ignition point) and also at 353 N in the friction test. According to the Regulations of the Japan Explosives Society[24], it was found that 1HT/PSANKN5 was classified as class 8 from the drop hammer test and as class 7 from friction test ; this mixture can be treated as an insensitive mixture.

4. Conclusions

The following conclusions were obtained for 1HT/PSANKN5 mixture.
1) It was found that adding more than 5 wt% of KNO_3 to AN, the transition temperature of AN near room temperature disappeared.
2) The melting point of 1HT/PSANKN5 was 377–391 K which was lower than the desirable 388 K.
3) The burning rate at 7 MPa was slightly higher than the desirable 10 mm·s^{-1}.
4) The rate of gas generation was approximately 1.4 times that for the GN/SrN/BCN mixture, which is a gas generant used in practical applications.
5) Based on the chemical equilibrium calculation, the gas generant generated harmless gases, and the efficiency of gas evolution, the wt% of solid products, the number of moles per 100 g of gas generant, and the calorific value per mole of generated gases were better than the desirable values. However, the adiabatic flame temperature and mol % of H_2O were higher than the desirable values.
6) The mixture was determined to be insensitive from drop hammer and friction tests.

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エアバッグ用ガス発生剤としての硝酸カリウム相安定化硝安と１HT混合物に関する研究

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　新規ガス発生剤について研究した。硝酸アンモニウムは有害ガスや固体残渣を発生しないが，室温付近に相転移温度があり，結晶系と密度の変化を起こして，ガス発生剤の形状を保つのが困難になる。この欠点を除くために硝酸カリウムを加えて相安定化した硝酸アンモニウムを用いた。5 wt%以上の硝酸カリウムを加えると室温付近の相転移のない相安定化硝安が得られた。燃料は，生成熱が大きく，窒素中で自己分解し，硝酸アンモニウムとの混合物が燃焼する１H-テトラゾールとした。融点，燃速，４Lタンク試験，各生成物量，ガス発生効率，固体残渣発生率，ガス発生剤100 g当たりのガス発生量，発生ガス１モル当たりの発熱量，感度などエアバッグ用ガス発生剤として望ましい特性について検討した。

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