Research paper

Equation for burning rate as a function of pressure and temperature for potassium nitrate-phase stabilized ammonium nitrate /1H-tetrazole mixture

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Abstract

The burning rate of propellants is affected by pressure and temperature. The relation between the burning rate and pressure has been well studied. However, the effect of the initial temperature on the burning rate has not been investigated quantitatively.

In this study, the burning rate of a phase stabilized ammonium nitrate containing potassium nitrate and 1H-tetrazole mixture was examined under conditions ranging from 1 to 10 MPa and 238 to 358 K, and an equation for the burning rate as a function of pressure and temperature was obtained. In general, the burning rates predicted by the correlation equation were in good agreement with the observed values. The temperature sensitivities were also predicted using the correlation equation and compared with the observed values and good agreement was found between the predicted and observed values.

Keywords : phase stabilized ammonium nitrate (PSAN), 1H-tetrazole, burning rate, initial temperature, temperature sensitivity

1. Introduction

The factors affecting the burning rate of propellants are pressure and temperature. The relation between the burning rate and pressure can be expressed by a Vieille's law. Much research has been conducted on the effect of initial temperature on the burning rates of rocket propellants[1)–9)] and airbag gas generating agents[10), 11)]. However, the effect of the initial temperature on the burning rate has not been investigated quantitatively. To obtain a temperature sensitivity-pressure diagram, we need an equation in differential form of the burning rate and the initial temperature. In previous studies, a second-order polynomial equation[4), 5), 10)] or a first-order equation[11)] was adopted. A second-order polynomial equation has a tendency to give higher or lower values when it is extrapolated to higher or lower temperatures. Therefore, a first-order equation was adopted in this study. To date, no equation for the burning rate based on temperature and pressure has been reported, except in our paper on 1H-tetrazole (1HT)/ammonium nitrate (AN)[11)]. If we can obtain such an equation, we will be able to calculate the burning rate under any conditions.

It is desirable for an airbag to maintain the time required for inflation, regardless of seasonal variations in temperature. If the temperature sensitivity of the burning rate is large, then the rate of air bag inflation would easily change with a temperature increase, which is undesirable. It is therefore desirable to have a low temperature sensitivity.

AN has attracted attention over the years as an environmentally friendly oxidizer for clean gas generating agents, because it does not give off harmful gases or solid burning residues, advantages that could fulfill the strict requirements imposed on gas generating agents for vehicle airbag systems. However, AN has the disadvantages that it is hygroscopic, which becomes a problem during manufacturing and storage, and also that it goes through contraction and expansion during phase transitions, which causes structural damage to the grains. There have been numerous studies related to these problems, and phase stabilization has been achieved by the addition of potassium nitrate (KN)[12)–15)]. In this study, phase stabilized ammonium nitrate (PSAN) was prepared by a nonhazardous aqueous method in which KN was added to AN. The amount of KN added was 5 wt%, which is the minimum amount necessary to accomplish the phase stabilization of AN (PSANKN)[16)].

AN alone is difficult to burn; i.e., AN has poor thermal and combustion reactivity. This means that AN-based gas generating agents prepared by mixing with organic fuels have low burning rates. It has been reported that aminoguanidinium 5,5'-azobis-1H-tetrazolate (AGAT)[10),17)], which decomposes by itself at approximately $1\ mm{\cdot}s^{-1}$ in a 1MPa N_2 atmosphere, can be used as a fuel to mix with AN. Preliminary experiments revealed that 1HT decomposes by itself at $5.52\ mm{\cdot}s^{-1}$ in a 1.1 MPa N_2 atmosphere, which suggests that 1HT can be used as a fuel with AN. The burning rate, 4-L tank test, and subjects which are desirable as gas generating agents were examined. Based on the study results, the 1HT/PSANKN mixture was found to satisfy the desired performances for air bag gas generating agents[16)].

2. Experimental

2.1 Materials

To obtain PSANKN, 190 g of AN and 10 g of KN were dissolved in a small amount of water; the solution was then heated to let the chemicals dissolve. The solution was placed in a 363 K thermostatic oven until it was completely dried. PSANKN and 1HT (Toyo Kasei Kogyo Co., Ltd.) were milled with a vibration ball mill and sieved through JIS Z8801 sieves and dried in a vacuum dryer. The particle sizes of PSANKN and 1HT were in the range of 75–150 μm. The ratio of 1HT to PSANKN was 23.43 : 76.57. Fuel particles and oxidizer particles were mixed at the designated mixing ratio for 30 min at 80 rpm using a rotary mixer.

2.2 Burning rate

A 1.5-g quantity of the stoichiometric 1HT/PSANKN mixture was compressed at approximately 300 MPa for 3 min to form cylindrical pellets (diameter 10 mm, length 11 mm). The side of the cylindrical pellet was coated with epoxy resin to assure cigarette burning. Combustion tests were performed using a pressure- and temperature-controlled chimney type strand burner with optical windows, under a N_2 atmosphere in the range of 1–10 MPa. The initial temperatures (T_i) were 238, 296, 323, and 358 K.

Ignition of the pellet was carried out with an 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. After amplification through a signal amplifier, the data were recorded using a digital data recorder. 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 the end of burning. The highest pressure difference was approximately 1.2 MPa for the arithmetic mean value of 9.9 MPa.

2.3 Temperature sensitivity

The 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[18)]. Variation of the burning rate per unit of temperature change at a constant pressure is called the temperature sensitivity of the burning rate at a constant pressure (σ_P)[18)], which can be expressed as

$$\sigma_P = \frac{(r_1 - r_0)}{r \cdot (T_1 - T_0)} \qquad (1)$$

where r_0 and r_1 are the burning rates at T_0 and T_1, respectively, and r is the average burning rate between T_0 and T_1. The unit of σ_P is K^{-1}. Equation (1) can be rewritten in a differential form

$$\sigma_P = \left(\frac{\partial\, ln\, r}{\partial T_i}\right)_P \qquad (2)$$

where σ_P can be obtained from Equation (2) by determining the relationship between r and T_i. A correlation equation between r and T_i was determined. Yang *et al*.[4)] and Miyata *et al*.[10)] adopted a second-order polynomial equation. However, in this study, a linear equation was used for T_i [Equation (3)], because it demonstrated a better correlation:

$$r = b_1(\mathrm{P}) \cdot T_i + b_0(\mathrm{P}) \qquad (3)$$

where $b_1(\mathrm{P})$ and $b_0(\mathrm{P})$ are functions of pressure. The change of airbag deployment rate with ambient temperature becomes smaller by reducing σ_P; therefore, it is desirable for σ_P to be small.

3. Results and discussion

3.1 Observed burning rate

The results of the burning rate tests of 1HT/PSANKN are presented in Figure 1 for initial temperatures of 238, 296, 323, and 358 K. The burning rates of 1HT/PSANKN follow Vieille's law and are shown by thin solid lines in Figure 1. The values of a and n at T_i are given in Table 1.

3.2 Equation for burning rate as a function of pressure and temperature

A regression analysis was conducted to derive an equation for obtaining a and n at any initial temperature.

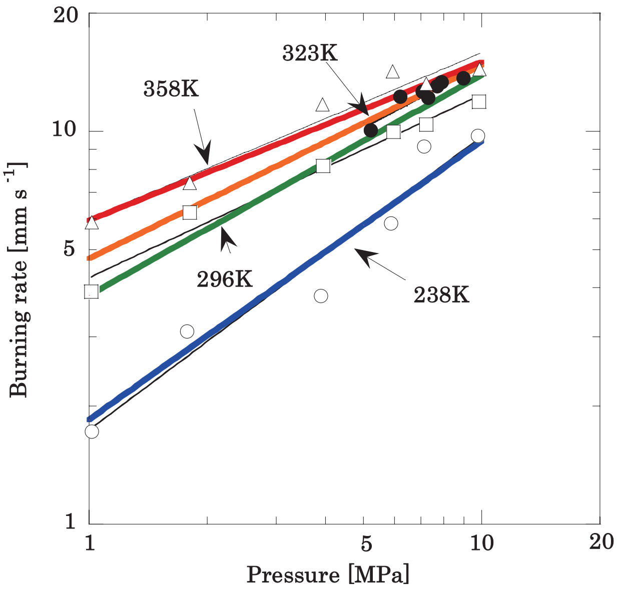

Figure 1 Burning rate for 1HT/PSANKN mixture at various initial temperatures.
Thin solid line (black) : $r = aP^n$
Bold solid line (colored) : Predicted by correlation formula

Table 1 Values of a and n for 1HT/PSANKN mixture at various temperatures.

Temperature [K]	a	n
358	5.9967	0.42304
323	4.3694	0.53278
296	4.2428	0.46604
238	1.737	0.74774

The relations between a and T_i, n and T_i are shown in Figure 2. The coefficient a increased linearly with T_i which is consistent with the findings of some other studies[1), 9)].

The pressure exponent n was in the range of 0.4 to 0.7 and the value of n decreased as T_i increased.

By a regression analysis, it was found that the burning rate could be expressed as $r = a_{reg} P^{n_{reg}}$, where a_{reg} and n_{reg} are a and n, respectively, for Vieille's law.

The value of a_{reg} can be expressed as $-6.2668 + 0.034085\, T_i$ and n_{reg} can be expressed as $1.3147 - 0.0025426 T_i$. Therefore, the burning rate can be expressed as

$$r = (-6.2668 + 0.034085 T_i) \cdot P \wedge (1.3147 - 0.0025426 T_i) \quad (4)$$

The burning rate can be predicted from Equation (4) at any initial temperature of 238–358 K and pressure of 1–10 MPa, respectively.

The observed and predicted burning rates are represented in Figure 1 as thin and bold solid lines, respectively. The burning rate values predicted from the correlation formula are in relatively good agreement with the observed burning rates for a wide range of initial temperatures and pressures, except for the high-pressure zone at 296 K.

The desirable burning rate for the airbag gas generating agents is higher than 10 mm·s^{-1} at 7 MPa[19]. At

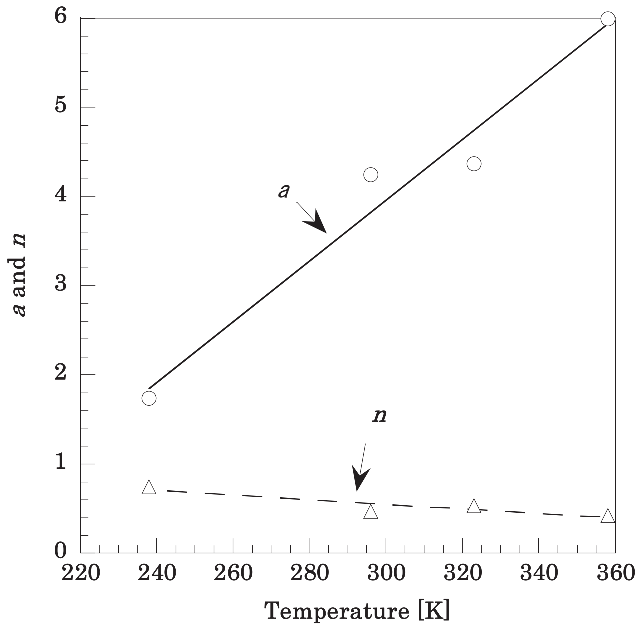

Figure 2 Relation between a, n and T_i for 1HT/PSANKN mixture.

7 MPa, the observed r was 11.4 mm·s^{-1}, which is higher than the desired value.

3.3 Temperature sensitivity

The burning rates from 1 to 10 MPa at various T_i were calculated by means of Vieille's law, $r = a \cdot P^n$, using values of a and n from Table 1. The relation between the calculated burning rates and T_i at different pressures is shown in Figure 3. Based on these relations, the coefficients of Equation (3) were determined for various pressures. The effect of temperature generally becomes more pronounced at higher pressures.

Table 2 shows the coefficients $b_1(P)$ and $b_0(P)$ of Equation (3)at various pressures.

The temperature sensitivities σ_P [computed from Equation (2)] versus P at various T_i are shown by solid lines in Figure 4. The values of σ_P decreased as P and T_i increased.

The results show that σ_P at 7 MPa was 4.91×10^{-3}K^{-1} when T_i was changed from 238 to 358 K.

The σ_P value is close to that of rocket propellants, 2×10^{-3} to 8×10^{-3}K^{-1} [17].

Table 2 Coefficients of Equation (3) determined at various pressures for 1HT/PSANKN mixture.

Pressure [MPa]	b_1(P)	b_0(P)
1	0.034085	−6.2668
2	0.041662	−6.8703
3	0.046027	−6.8758
4	0.048863	−6.6127
5	0.050782	−6.196
6	0.052082	−5.6805
7	0.052935	−5.0964
8	0.053448	−4.4624
9	0.053692	−3.7907
10	0.053719	−3.0899

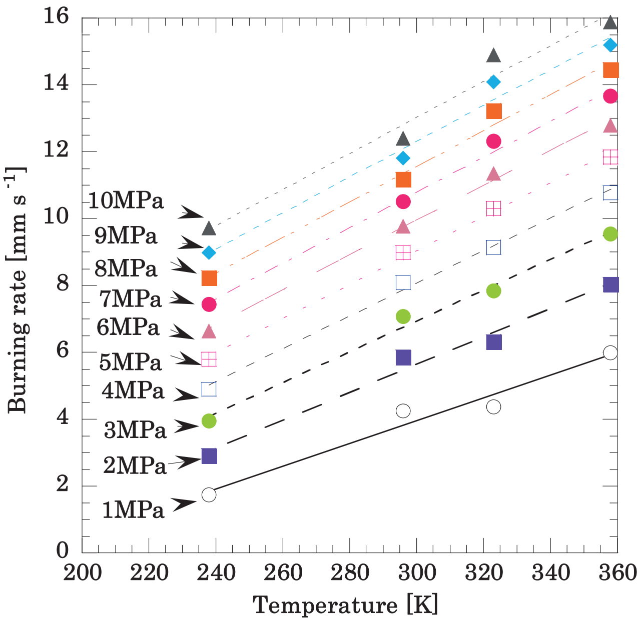

Figure 3 Burning rate as a function of temperature at various pressures for 1HT/PSANKN mixture.

Table 3 Values of A and B for $\sigma_{per} = A \cdot P^B$ at various temperatures for 1HT/PSANKN mixture.

Temperature [K]	A	B
358	0.0060392	−0.2386
323	0.0075941	−0.28271
296	0.0094539	−0.33019
238	0.019449	−0.52453

At 7 MPa, the predicted burning rates (r_{pre}) using Eq. (4) at 238 and 358 K were 7.34 and 13.04 mm·s^{-1}, respectively, and σ_P was 4.66×10^{-3}K^{-1} which is relatively close to the observed value.

3.4 Equation for temperature sensitivity as a function of pressure and temperature

The relationships between temperature sensitivity and P and T_i were investigated. The predicted temperature sensitivity (σ_{pre}) can be expressed by the following equation[4), 10), 11)]

$$\sigma_{pre} = A \cdot P^B \qquad (6)$$

where $A = K_1 + K_2 \cdot T_i + K_3 \cdot T_i^2$ and $B = K_4 + K_5 \cdot T_i + K_6 \cdot T_i^2$. At various T_i, A and B were obtained for the solid lines in Figure 4; results are given in Table 3. Regression analyses were conducted for A and B as shown in Figure 5, and the obtained coefficients $K_1 - K_6$ are given in Table 4.

The bold dashed lines in Figure 4 indicate the results derived from Equation (6).

These results show that σ_{pre} coincides with σ_P. Therefore, the correlation formula can be successfully used to predict temperature sensitivity over a wide range of pressures and temperatures.

4. Conclusions

This study evaluated the possibility of predicting the burning rates of patassium nitrate-phase stabilized ammonium nitrate /1H-tetrazole mixture at any initial temperature and pressure.

An equation was obtained for the burning rate as a function of pressure and temperature after using a regression analysis to obtain the relation between the

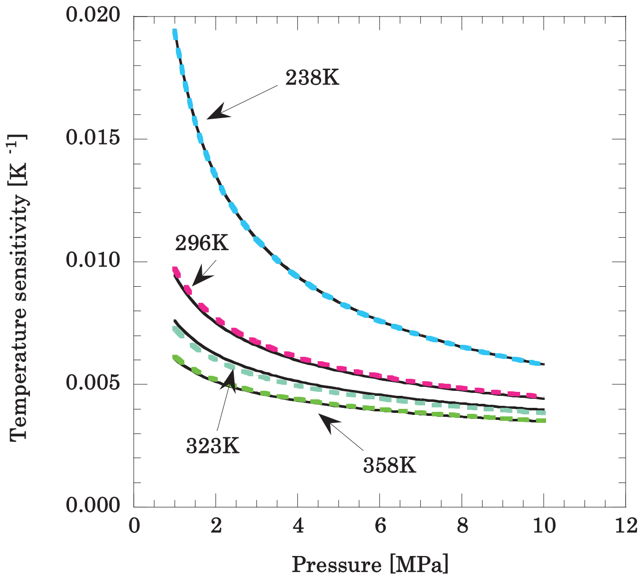

Figure 4 Temperature sensitivity and predicted temperature sensitivity for 1HT/PSANKN mixture.
Bold dashed line : Predicted
Solid line : Observed

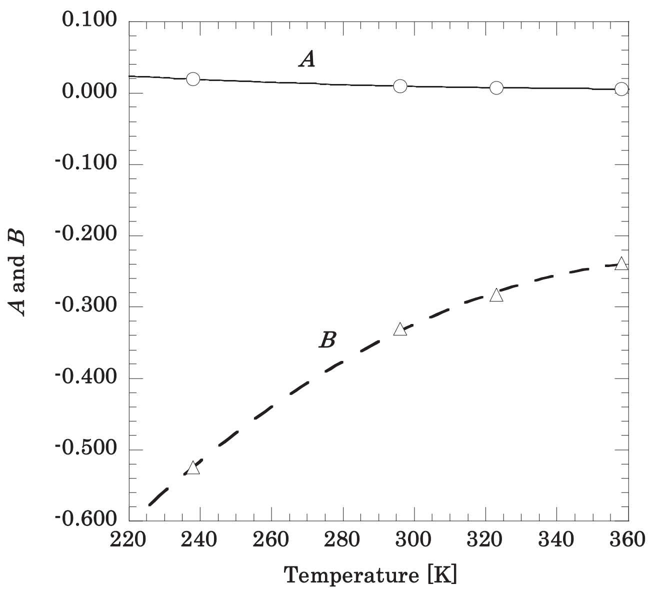

Figure 5 Regression analysis of A and B for $\sigma_{per} = A \cdot P^B$.

Table 4 Values for coefficients K_1 through K_6 for 1HT/PSANKN mixture.

	1HT/PSANKN
K_1	1.2356×10^{-1}
K_2	-6.5499×10^{-4}
K_3	9.1338×10^{-7}
K_4	-2.3472
K_5	1.1179×10^{-2}
K_6	-1.4783×10^{-5}

initial temperature and a or n in Vieille's law, as given by $r = aP^n$.

In general, the calculated burning rate was in good agreement with the observed values.

The prediction of temperature sensitivity by the correlation formula is generally successful over a wide range of pressures and temperatures.

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硝酸カリウム相安定化硝酸アンモニウムと1H-テトラゾール混合物の温度と圧力を関数とする燃焼速度式

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燃焼速度に影響する因子には圧力と温度がある。燃焼速度と圧力の関係は良く研究されているが，燃焼速度と温度の関係の定量的報告は少ないようである。本実験では硝酸カリウムで相安定化した硝酸アンモニウムと1H-テトラゾールの混合物について，燃焼速度に及ぼす圧力と温度の関係を調べ，圧力と温度を変数とする燃焼速度式を得た。得られた燃焼速度式から計算した燃焼速度は，実験値と広い範囲で良く一致した。また，温度感度についても相関式から得た値と実験値から得られた値が良く一致した。

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