Research paper

Three-dimensional diagrams for burning rate and temperature sensitivity as a function of pressure and temperature for a guanidine nitrate / strontium nitrate / basic copper nitrate mixture

Kazuo Hasue*† and Kazuya Yoshitake**

*Department of Applied Chemistry, School of Applied Sciences, National Defense Academy (ret.)
1-10-20, Hashirimizu, Yokosuka, Kanagawa 239-8686, JAPAN
Phone : +81-46-841-3810
† Corresponding author : khasue@hotmail.com

**JDSDF Test and Evaluation Command 481-27, Subashiri, Oyama, Shizuoka 410-1431, JAPAN

Received : May 7, 2014 Accepted : September 25, 2014

Abstract

The burning rate of energetic materials 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. The burning rate of a guanidine nitrate / strontium nitrate / basic copper nitrate mixture was examined and an equation for the burning rate as a function of pressure and temperature was obtained. The predicted burning rates were in good agreement with the observed values. The temperature sensitivities were also predicted using the regression equation and compared with the observed values and good agreement was found. The three-dimensional diagrams of the burning rate and the temperature sensitivity are presented. Without complicated calculations, the burning rate and the temperature sensitivity can be predicted at any pressure and temperature within the range of study.

Keywords : temperature sensitivity, regression analysis, guanidine nitrate, strontium nitrate, basic copper nitrate

1. Introduction

To obtain the burning rate is the principal objective of the combustion study of energetic materials. The factors affecting the burning rate of energetic materials are pressure and temperature. The burning rates (r) 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 an initial temperature of the energetic materials, and n is the pressure exponent of the burning rate and P is the pressure[1].To evaluate the performance of energetic materials, the relation between the burning rate and pressure has been well-studied.

Much research has been conducted on the effect of initial temperature on the burning rates of rocket propellants[2)-10)] and airbag gas generating agents[11)-17)]. However, the effect of the initial temperature on the burning rate has not been investigated quantitatively except the authors' reports[14)-17)].

We need an equation in differential form of the burning rate and the initial temperature to obtain a temperature sensitivity-pressure diagram. In previous studies, a second-order polynomial equation[6),7),11),12)] or a first-order equation[14)-17)] has been adopted. A second-order polynomial equation has a tendency to give higher or lower burning rate values when it is extrapolated to higher or lower temperatures. This tendency does not agree with the Arrhenius equation of which the burning rate increases with an increase in temperature. 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 papers[14)-17)]. If we can obtain such an equation, we will be able to estimate the burning rate at any initial temperature and pressure.

The temperature sensitivity of the burning rate is one of the important parameter for energetic materials. The temperature sensitivities based on the predicted burning rates have been calculated and compared with the observed values[14)−17)].

We have already reported on the burning rate equations for 1HT / AN mixtures mixture[14)], phase stabilized ammonium nitrate containing potassium nitrate /1HT mixture[15)], BTA·NH_3 / PSAN mixture[16)], and 1HT / CuO / additive mixtures[17)].

In this study, guanidine nitrate (GN ; Kanto chemicals co. inc.) was selected as a fuel because it has a high gas output and low flame temperature. Strontium nitrate (SrN ; Kanto chemicals co. inc.) and basic copper nitrate (BCN ; Nihon kagaku sangyo co., ltd.) were selected as oxidizers. The mixture is one of the gas generant candidates[18)].

2. Experimental

2.1 Materials

GN and SrN were dried in vacuum and sieved. The particle sizes of GN and SrN were in the range of 75−149 μm and BCN was used as received. GN, SrN, and BCN were mixed in a ratio of 56.06 : 19.45 : 24.50 (w / w) for 30 min at 80 rpm using a rotary mixer (S−3, Tsutsui scientific instruments co. ltd.).

2.2 Burning rate

One and half grams of GN / SrN / BCN mixture was compressed at approximately 300 MPa for 3 min to form cylindrical pellets (diameter 10 mm, length 9 mm). The side of the cylindrical pellet was coated with epoxy resin to assure cigarette-like burning. Combustion tests were performed using a pressure- and temperature-controlled chimney-type strand burner with optical windows (TDK−15011, Tohata denshi co. ltd.), under N_2 atmosphere in the range of 1−10 MPa. The initial temperatures (T_i) were 238, 296, 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 (QP035−20R, Takasago ltd.). The pressure in the chamber was measured with a pressure sensor (AP15S, Keyence corp.). After amplification through a signal amplifier (AP−V85, Keyence corp.), the data were recorded using a digital data recorder (GR−3000, Keyence corp.).

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. From the acquired pressure-time data, as shown schematically in Figure 1, the burning rates (r) were deduced from the duration of the recorded pressure increase. An example of the highest pressure difference will be given ; for the arithmetic mean value of 9.90 MPa, the starting pressure was 9.31 MPa and the ending pressure was 10.48 MPa. All measurements were conducted once at each pressure and temperature.

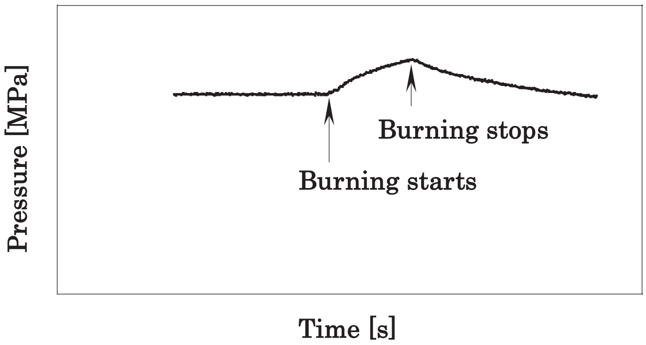

Figure 1 Schematic diagram of pressure-time history from burning rate measurement.

2.3 Temperature sensitivity

Variation of the burning rate per unit of temperature change at a constant pressure is called the temperature sensitivity of burning rate at a constant pressure (σ_P)[1)], which can be expressed as

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

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.

Equation 1 can be rewritten in a differential form

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

σ_P can be obtained from Equation 2 by determining the relationship between r and T_i. A regression equation between r and T_i was determined ; in this study, a linear equation for T_i is

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

where $b_1(P)$ and $b_0(P)$ are functions of pressure.

3. Results and discussion

3.1 Observed burning rate

The results of the burning rate tests for the GN / SrN / BCN are presented in Figure 2 for T_i of 238, 296, and 358K. The observed burning rates (r) are seen to follow Vieille's law, as indicated by the black lines in Figure 2.

3.2 Burning rate equation as a function of pressure and temperature

The fitting results for the Vieille's law, $r = a \cdot P^n$, are summarized in Table 1. The correlation coefficients of the equation for the mixture were in the range of 0.990−0.996 (0.917 at the 0.01 significance level[19)]) and, consequently, the data correlate well according to the equation.

A regression analysis was conducted to derive an equation for obtaining a and n at any T_i within the range of study. The relations between a and T_i and n and T_i are shown in Figure 3. The constant (a) increased as T_i increased. The correlation coefficient was 0.994. The pressure exponent (n) was almost independent of T_i.

It was found by a regression analysis that the predicted burning rate (r_{pre}) can be expressed as $r_{pre} = a_{reg} P^{n_{reg}}$,

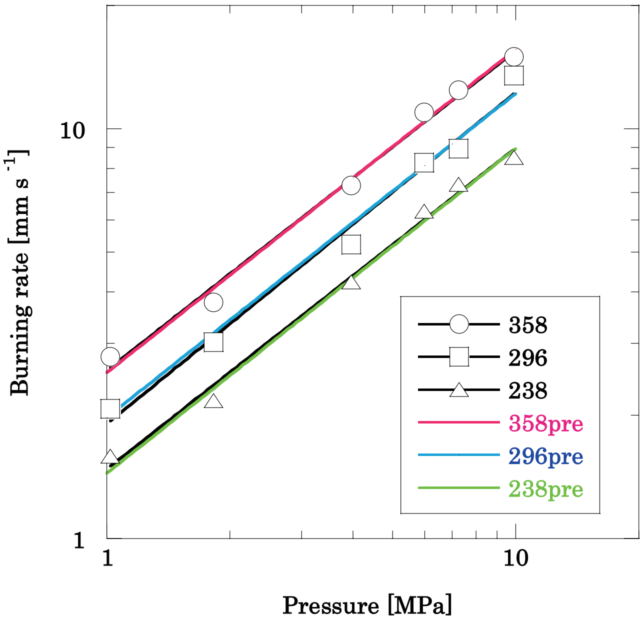

Figure 2 Burning rate for a GN / SrN / BCN mixture at various initial temperatures.
Black line : $r = aP^n$
Colored line : Predicted by a regression equation

Table 1 Fitting results of $r = aP^n$ for a GN / SrN / BCN mixture.

Initial temperature [K]	a [mm s^{-1}MPa^{-1}]	n [−]	Correlation coefficient
358	2.574	0.7800	0.996
296	1.906	0.8091	0.990
238	1.478	0.7833	0.995

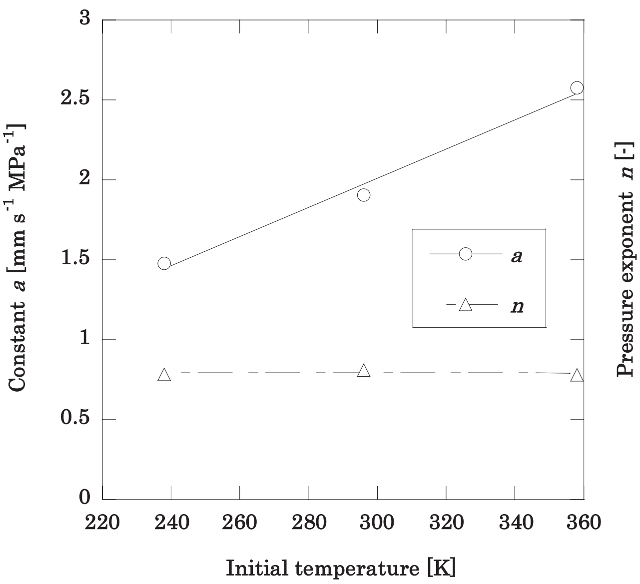

Figure 3 Relation between a, n, and initial temperature for a GN / SrN / BCN mixture.
a : Constant, n : Pressure exponent

where a_{reg} and n_{reg} are a and n for Vieille's law, respectively. The value of a_{reg} can be expressed as $-0.7350+0.009152 \cdot T_i$ and n_{reg} can be expressed as $0.8007-0.00003315 \cdot T_i$. Therefore, the burning rate can be expressed as

$$r_{pre} = (-0.7350+0.009152 \cdot T_i) \cdot P^{(0.8007-0.00003315 \cdot T_i)} \quad (4)$$

The burning rate can be predicted from Equation 4 for any T_i and P within the range of study. The observed and predicted burning rates are represented in Figure 2 as black lines and colored lines, respectively. The burning rate values predicted from the regression equations are in relatively good agreement with the observed burning rates for a wide range of T_i and P.

A three-dimensional diagram of the burning rate predicted from Equation 4 in the range of 230−360 K and 1 −10 MPa is shown in Figure 4. Without a complicated calculation, the burning rate can be predicted. The burning rate (r) increases as P and T_i increase. Gas generant generally requires a burning rate of at least 10 mm s^{-1} or more at 7MPa[20]. According to Figure 4, the composition gave approximately 9 mm s^{-1} at 7MPa and 300 K.

3.3 Temperature sensitivity

The burning rate is dependent on pressure and temperature. The dependency of the burning rate on the pressure is expressed as Vieille's law at a given temperature. On the other hand, the dependency of the burning rate on the initial temperature can be expressed as the temperature sensitivity.

The burning rates from 1 to 10 MPa at each 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 r and T_i at various pressures are shown in Figure 5. The burning rate (r) increases with an increase in T_i. The relation between r and T_i was found to be a first-order equation. Based on these relations, the coefficients $b_1(P)$ and $b_0(P)$ of Equation 3 were determined for various pressures and then we can calculate the temperature sensitivity. 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 from 1 to 10 MPa at various T_i are shown by solid lines in Figure 6. The values of σ_P decreased as P and T_i increased.

According to Miyata et al[12], σ_P decreases with an increase in P when σ_P in the condensed phase is dominating. In contrast, in situations where σ_P increases with an increase in P, σ_P in the gas phase is dominating. The temperature sensitivity σ_P decreases with an increase in P, therefore, σ_P in the condensed phase is dominating.

The predicted burning rate (r_{pre}) was obtained by using Equation 4 and then the coefficients $b_1(P)$ and $b_0(P)$ of Equation 3 were determined for various pressures. We can obtain σ_{pre} shown by dashed lines in Figure 6. There is good agreement between σ_{pre} and σ_p.

3.4 Temperature sensitivity as a function of pressure and temperature

The relationships between temperature sensitivity and P and T_i were investigated. The predicted temperature

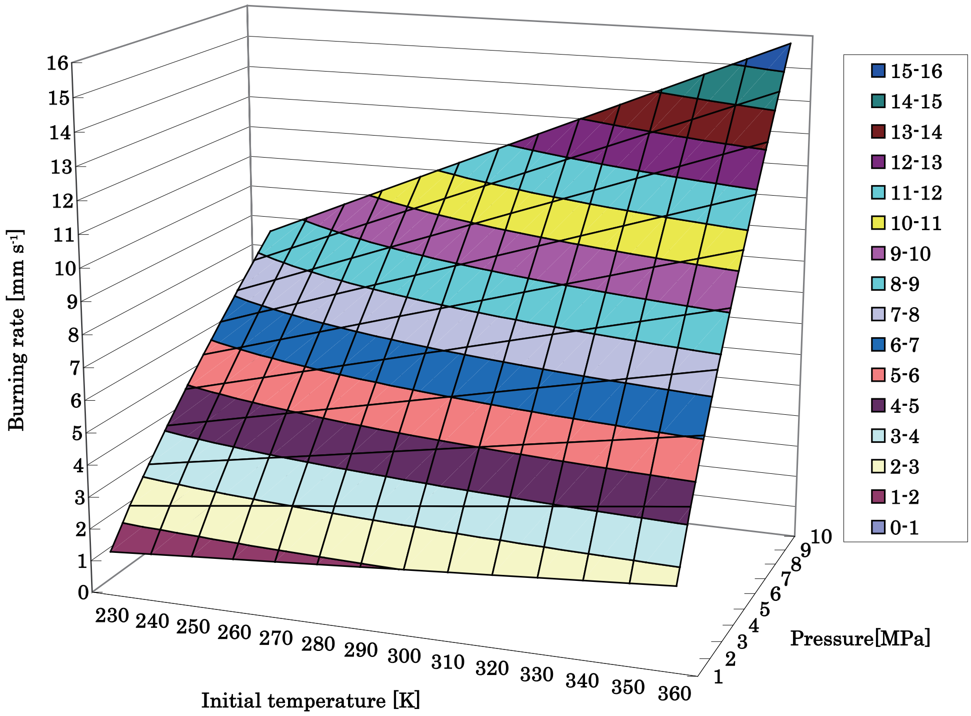

Figure 4 Three dimensional diagram for burning rate as a function of pressure and temperature for a GN / SrN / BCN mixture.

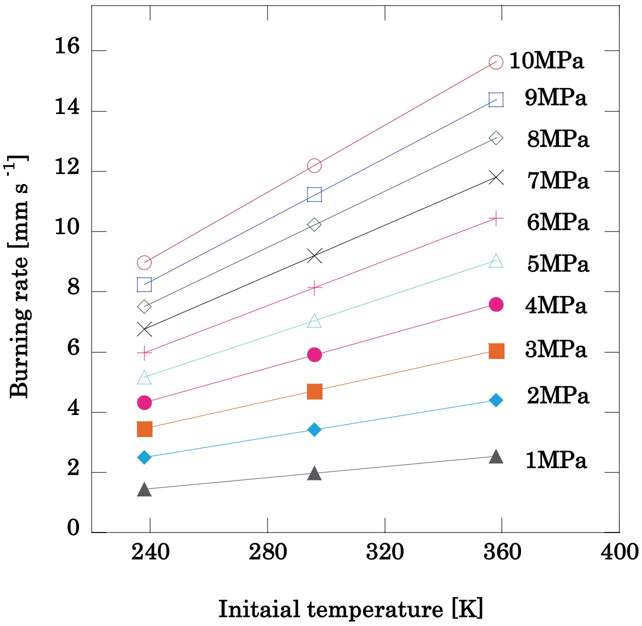

Figure 5 Burning rate as a function of initial temperature at various pressures for a GN / SrN / BCN mixture.

sensitivity (σ_{pre}) can be expressed by the following equation[6), 12)].

$$\sigma_{pre} = A \cdot P^{B} \tag{5}$$

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 dashed lines in Figure 6; results are given in Table 3. Regression analyses were conducted for A and B as shown in Figure 7 and 8, respectively and the obtained coefficients $K_1 - K_6$ are given in Table 4.

Therefore, σ_{pre} can be expressed as

Table 2 Coefficients $b_1(P)$ and $b_0(P)$ of Equation 3 determined at various pressures for a GN / SrN / BCN mixture.

Pressure [MPa]	$b_1(P)$	$b_0(P)$	$b_1(P)^*$	$b_0(P)^*$
1	0.009152	−0.7349	0.009152	−0.7350
2	0.01565	−1.219	0.01575	−1.249
3	0.02143	−1.639	0.02165	−1.702
4	0.02677	−2.020	0.02712	−2.121
5	0.03182	−2.376	0.03230	−2.515
6	0.03665	−2.712	0.03726	−2.891
7	0.04129	−3.032	0.04204	−3.252
8	0.04579	−3.340	0.04667	−3.601
9	0.05016	−3.637	0.05119	−3.940
10	0.05442	−3.925	0.05559	−4.270

*: Based on the predicted burning rates by means of Equation 4.

$$\sigma_{pre} = (0.02080 - 0.00008593 \cdot T_i + 0.0000001059 \cdot T_i^2) \cdot P^{(-0.03103 + 0.0001277 \cdot Ti - 0.0000001569 \cdot Ti^2)} \tag{6}$$

A three-dimensional diagram of the temperature sensitivity predicted from Equation 6 in the range of 230−360 K and 1−10 MPa is shown in Figure 9. Without a complicated calculation, σ_{pre} can be predicted.

4. Conclusion

This study evaluated the possibility of predicting the burning rates of guanidine nitrate / strontium nitrate / basic copper nitrate mixture at any initial temperature and pressure within the range of study.

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

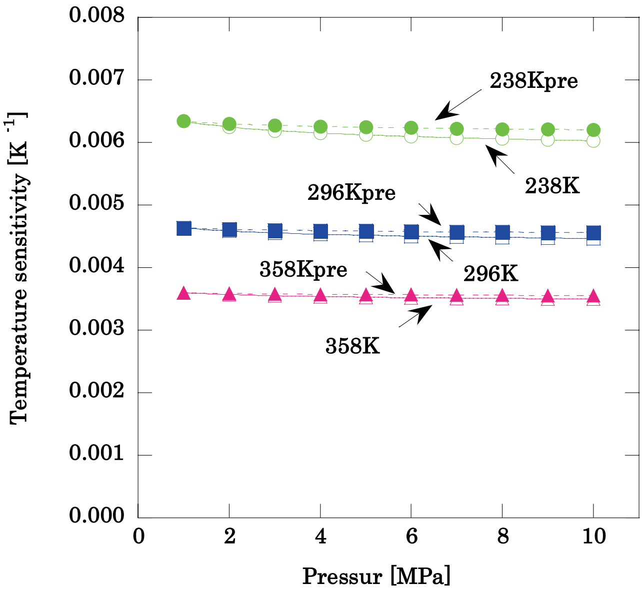

Figure 6 Temperature sensitivity and predicted temperature sensitivity for a GN / SrN / BCN mixture.
Solid line : Observed
Dashed : Predicted

Table 3 Values of A and B for $\sigma_{pre} = A \cdot P^B$ at each temperature.

Temperature [K]	A	B
358	0.003601	−0.005444
296	0.004636	−0.006996
238	0.006342	−0.009540

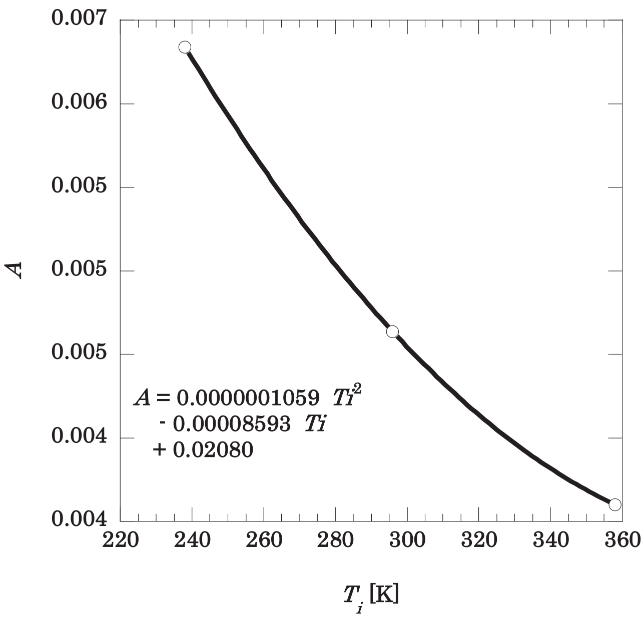

Figure 7 Regression analysis of A for $\sigma_{pre} = A \cdot P^B$.

initial temperature and a or n in Vieille's law, as given by $r = aP^n$. In general, the predicted burning rates were in good agreement with the observed values.

The prediction of temperature sensitivity from the predicted burning rate, using a burning rate equation based on pressure and temperature is successful over a wide range of pressures and temperatures.

The three-dimensional diagrams of the burning rate and the temperature sensitivity are presented. Without complicated calculations, the burning rate and the temperature sensitivity can be predicted at any pressure and temperature.

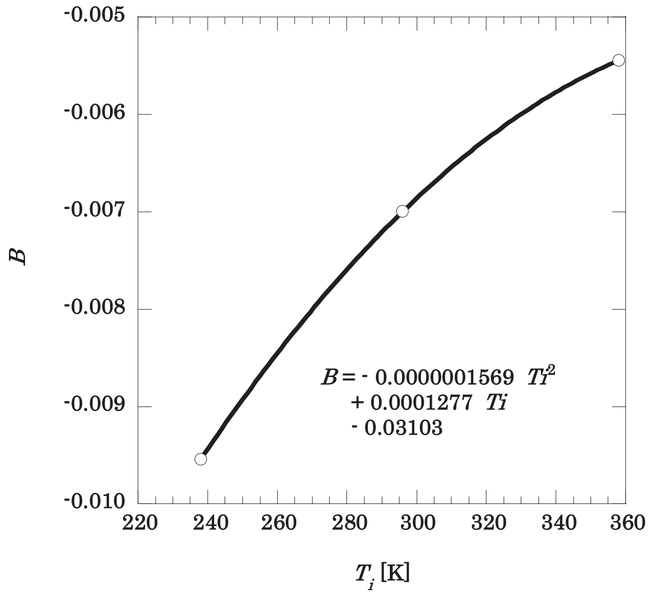

Figure 8 Regression analysis of B for $\sigma_{pre} = A \cdot P^B$.

Table 4 Values for coefficients K_1 through K_6.

Sample	GN / SrN / BCN
K_1	0.02080
K_2	−0.00008593
K_3	0.0000001059
K_4	−0.03103
K_5	0.0001277
K_6	−0.0000001569

References

1) N. Kubota, "Propellants and Explosives-Thermochemical Aspects of Combustion", 53–54, WILEY-VCH (2002).
2) R. L. Glick, AIAA Journal, 5, 586–587 (1967).
3) N. Kubota and A. Ishihara, Proc. 20th Symposium (International) on Combustion, 2035–2041, The Combustion Institute, Ann Arbor, MI, USA, (1984).
4) N. S. Cohen and D. A. Flanigan, AIAA Journal, 23, 1538–1547 (1985).
5) N. Kubota and S. Miyazaki, Propellants, Explos., Pyrotech., 12, 183–187 (1987).
6) A. S. Yang, I. H. Huang, W. H. Hsieh, and K. K. Kuo, "Combustion of Boron-Based Solid Propellants and Solid Fuels", 412–426, CRC Press (1993).
7) R. M. Salizzoni , W. H. Hsieh, and K. K. Kuo, *ibid*., 438–452.
8) I. Aoki, Kayaku Gakkaishi (Sci. and Tech. of Energetic Materials), 59, 36–43 (1998) (in Japanese).
9) A. I. Atwood, T. L. Boggs, P. O. Curran, T. P. Parr, and D. M. Hanson-Parr, J. Prop. Power, 15, 748–752 (1999).
10) V. V. Kulkarni, A. R. Kulkarni, P. A. Phawade, and J. P. Agrawal, Propellants, Explos., Pyrotech., 26, 125–129 (2001).
11) H. Bazaki , T. Kai, and T. Anan, Kayaku Gakkaishi (Sci. and Tech. of Energetic Materials), 57, 153–159 (1996) (in Japanese).
12) Y. Miyata and K. Hasue, J. Energ. Mater., 29, 26–45 (2011).

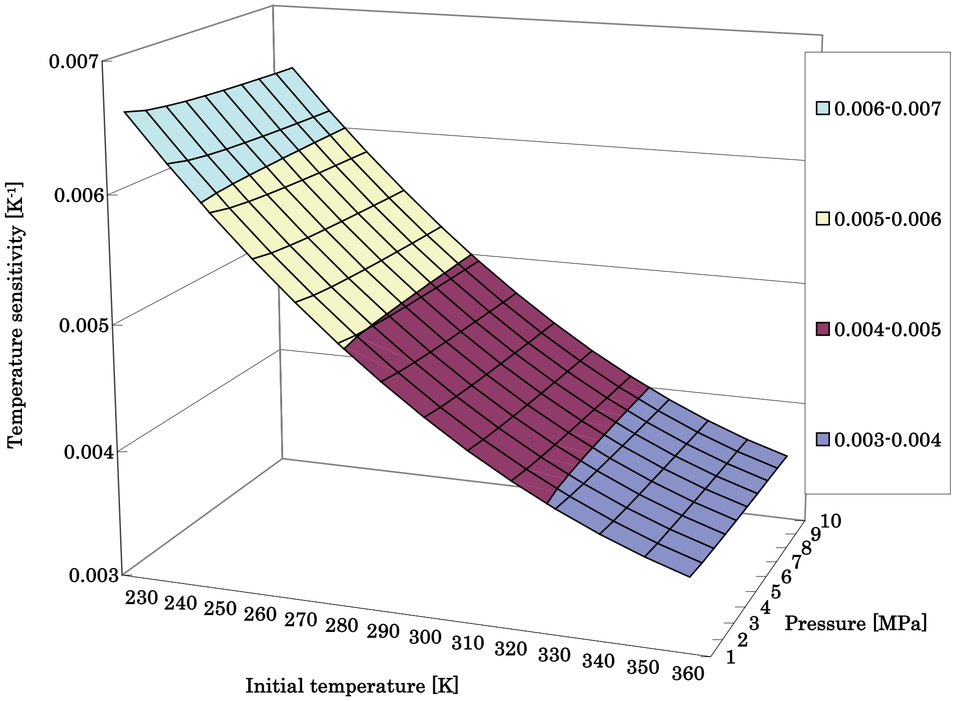

Figure 9 Three dimensional diagram for temperature sensitivity as a function of pressure and temperature for a GN / SrN / BCN mixture.

13) K. Yositake, K. Ihoh, S. Date, and K. Hasue, Proc. 36th International Pyrotechnics Seminar, International Pyrotechnics Society, 287−301, Rotterdam, Netherlands (2009).

14) K. Hasue and K. Yoshitake, J. Energ. Mater., 31, 251−260 (2013).

15) K. Hasue, R. Miura, and K. Yoshitake, Sci. Tech. of Energetic Materials, 74, 113−117 (2013).

16) K. Hasue, J. Energ. Mater., 32, 199−206 (2014).

17) M. Matsukawa and K. Hasue, *ibid*, 32, 264−277 (2014).

18) E. Sato, D. Kubo, and K. Ikeda, U. S. Patent, 6958100B2 (2005).

19) Radford University, "Table of Critical Values for Pearson's r", http://www.radford.edu/ jaspelme/statsbook/Chapter files/ Table_of_Critical_Values_for_r.pdf, (accessed : 20−September−2014)(online).

20) P. S. Khandhadia and S. P. Burns, U. S. Patent, 6306232B1 (2001).