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Mathematical and Experimental Study for Mixed Energetic Materials Combustion in Closed System

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Abstract – Modelling the energy release performance of energetic material combustion in closed systems is of fundamental importance for aerospace and defense application. In particular, to compensate for the disadvantage of the combustion of single energetic material and maximize the benefits, a method of combusting the mixed energetic materials is used. However, since complicated heat transfer occurs when the energetic material is combusted, it is difficult to theoretically predict the combustion performance. Here, we suggest a theoretical model to estimate the energy release performance of mixed energetic material based on the model for the combustion performance of single energetic material. To confirm the effect of parameters on the model, and to gain insights into the combustion characteristics of the energetic material, we studied parameter analysis on the reaction temperature and the characteristic time scales of energy generation and loss. To validate the model, model predictions for mixed energetic materials are compared to experimental results depending on the amount and type of energetic material. The comparison showed little difference in maximum pressure and the reliability of the model was validated. Finally, we hope that the suggested model can predict the energy release performance of single or mixed energetic material for various types of materials, as well as the energetic materials used for validation.

Key words: Mathematical modelling, Energetic material, Combustion, Unsteady heat transfer

1. Introduction

The energy release performance that occurs when energetic materials combust plays an important role in the successful launch, manipulation, operation and separation of launchers in the aerospace and defense industries [1-6]. When energetic materials combust in a closed system, a large amount of energy is generated, and the temperature rises rapidly and complex heat transfer occurs inside the system. In addition, these energy releases occur within a very short time (< 0.2 ms), and it is difficult to analyze the system theoretically because both molecular and macroscopic viewpoints must be considered. Because of this complexity and difficulty, most of the existing models describe the performance by using Vieille's law (or Saint Robert's law, $R = aP^n$), which explains the combustion reaction rate (or burning rate) as a function of pressure [7].

There are researches to determine the value of coefficient (a) and exponent (n) for energetic material or make mathematical models from Vieille's law to explain the performance of energetic material [7-9]. However, these models involve some technical problems that require unknown coefficients and exponents, which are fitted from experiments under various constant pressure conditions. Because Vieille's law is an empirical formula, the values of parameters change, according to the experimental conditions, even with the same material. This change makes the performance of the model depend on the parameter values adopted from the literature. In addition, since the microscopic informations such as chemical composition and reaction heat of the energetic material are lumped in macroscopic parameters a and n, it is necessary to determine the parameter value through experiments when the type or relative amount of energetic material changes. Furthermore, Vieille's Law measures the reaction rate under constant pressure conditions such as an open system, a theoretical model is necessary to describe a closed system where the pressure is unsteady.

Yang theoretically determined the reaction rate of various energetic materials by the characteristic heat transfer time which is derived from the one-dimensional heat transfer, based on cubic unit cell model from a molecular perspective [10,11]. Because this model includes the thermodynamic characteristics of the chemical reaction and energetic material composition from a microscopic viewpoint, the perspective can be extended to various materials. However, although this model can theoretically explain the performance of energetic material itself, it cannot validate the results by comparison with real energetic material performance, because it doesn't have

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‡This paper is dedicated to the retirement of Professor In-seok Kang of Pohang University of Science and Technology.

any system, such as closed bomb test (CBT or closed vessel test). Therefore our previous study, to theoretically evaluate the energy release performance of energetic material combustion, suggested a mathematical model based on the cubic unit cell model and CBT system to evaluate the performance of ZPP (Zirconium Potassium Perchlorate) [12]. Because the CBT system was used, the heat loss from the system was also considered to estimate precise performance. However, because the model evaluated the performance of ZPP only, it is necessary to modify the model to evaluate the performance of mixed energetic materials, and to apply the model to various types of energetic materials.

Therefore, in this study, the view was expanded to theoretically predict the combustion performance of two mixed energetic materials as well as single energetic materials. Additionally, parametric analysis was conducted for model parameters containing the chemical compositional properties and thermodynamic characteristics of the energetic material, and the physical characteristics of the system. In order to understand the characteristics of energetic material with minimal experimentation, the effects of each independent parameter of the model on the performance were analyzed and systematically validated the important factors affecting the energetic material combustion. We theoretically applied the model to THPP (Titanium Hydride Potassium Perchlorate) and $BKNO_3$ (Boron Potassium Nitrate), as well as ZPP, and predicted the performance of mixed energetic materials. The model predictions for the mixed energetic materials were compared with the CBT experimental data. The accuracy and applicability to various energetic materials of the suggested model were validated by changing the amount of each material. In addition, the time delay that can occur in mixed energetic materials was systematically validated by comparison and analysis with experimental data using the model. Through this study, it is expected that the suggested model can be applied to other types of single or mixed energetic materials, as well as the materials mentioned above.

2. Mathematical Model

2-1. Single Energetic Material Energy Release Model

Fig. 1 shows an overview of the CBT process, which is mainly used to evaluate the energy release performance of energetic material. The closed bomb filled with energetic materials contains an initiator and a pressure sensor. When the bomb is heated through the conduction wire included in the initiator, within a very short time (< 0.2 ms), the internal temperature becomes the ignition temperature of the energetic material, and the molecules forming the energetic material initiate the redox reaction to release the energies, and produce combustion gases.

In the CBT system, the energy change inside a closed bomb involves two steps: (1) energy generation due to exothermic reaction of energetic materials, and (2) energy loss through the wall of the closed bomb. Based on this observation, in our previous study, the energy release performance when single energetic material is combusted in a closed bomb is expressed as shown in Eq. (1) [12].

$$P(t)=\frac{R'}{(v-b)}\left[T_0+(T_r-T_0)erfc\sqrt{\frac{t_1}{4t}}-\frac{hA}{mC_v}(T_r-T_0)erfc\sqrt{\frac{t_2}{4t}}\right] \quad (1)$$

The above model shows the change of energy released when the single energetic material combusts in a closed bomb as a form of pressure change over time.

2-2. Mixed energetic materials energy release model

In this study, the model describing the energy release performance of a single energetic material has been expanded to account for the energy release performance of mixed energetic materials combustion. Fig. 1 shows that the mixed energetic materials combust in the same bomb. By the law of energy conservation, the sum of the energy of the system (here the bomb) can be obtained from the energy generated in the system, and the energy lost to the surroundings from the system. If there is no interaction between the mixed energetic materials, the energy generation, $E_G(t)$ and energy loss, $E_L(t)$ of the system can be obtained as the sum of energy generation and loss in each energetic material, as shown in the following Eq. (2), where subscripts 1 and 2 represent two different energetic materials. Therefore, the energy change, $E(t)$ of the mixed energetic materials can be expressed by adding the energy change of each energetic material:

$$\begin{aligned}E(t)&=E_G(t)-E_L(t)=E_{1,G}(t)+E_{2,G}(t)-[E_{1,L}(t)+E_{2,L}(t)]\\&=E_1(t)+E_2(t)\end{aligned} \quad (2)$$

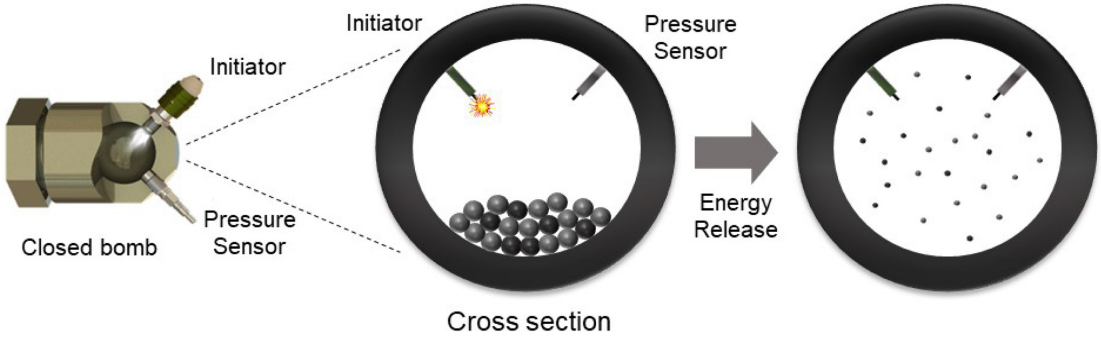

Fig. 1. Schematics of a closed bomb test (CBT) combustion system.

The given model explains the performance of energetic material as a pressure change. Pressure is the amount of energy per unit volume, which can be obtained by dividing the energy of the entire system by its volume. The suggested model calculates the pressure using the Noble-Abel EOS given in the second term of the following Eq. (3), instead of the ideal gas EOS [13].

$$P = \frac{R'T}{(v-b)} = \frac{mR'T}{M(v-b)} = \frac{mR'T}{(V-b')} = \frac{nRT}{(V-b')} = \frac{E}{(V-b')} \quad (3)$$

Here, R' is a gas constant a gas constant divided by the molecular weight of the gas. In this case, the denominator of the second term represents the volume per unit mass of the system, excluding the volume occupied by the gas (b), namely, the specific volume (v), not the total volume (V). If the numerator and denominator in the second term are multiplied by mass (m), it can be expressed as the third term ($b' = mb$). Here, the numerator represents the total energy, and the denominator represents the net total volume, which excludes the volume occupied by the combustion gas molecules from the total volume. From Eq. (3), it is possible to calculate the pressure, by dividing the total energy of gas molecules by the net total volume. The total energy change of the mixed energetic materials can be expressed as Eq. (4), as the sum of the energy change of each component energetic material by Eqs. (2) and (3):

$$E(t) = E_1(t) + E_2(t) = m_1 R_1' T_1(t) + m_2 R_2' T_2(t) \quad (4)$$

To calculate the pressure of mixed energetic material, it is important to determine the b' of mixed energetic material in the denominator. The combustion gases of each energetic material exist in the same bomb simultaneously. That is, the mixed energetic materials are affected by all combustion gases generated from each energetic material. Under no reaction between the combustion gases, the volume of the gases produced from the mixed energetic materials can be expressed as the sum of the volume of the gases generated from each energetic material, $b' = m_1 b_1 + m_2 b_2 = b_1' + b_2'$. Therefore, the pressure change of the mixed energetic materials can be obtained as shown in Eq. (5), by dividing the total energy change of the mixed energetic materials calculated from Eq. (4) by the net total volume of the mixed energetic materials, $V\text{-}b'$. As a result, applying the total net volume to each energetic material considering the total combustion gas generated from each energetic material, the total pressure change $P(t)$ can be obtained by adding the pressure change of each component energetic material $P_1(t) + P_2(t)$. Here, it should be noted that $P_1(t) = E_1(t)/(V\text{-}b')$, not $E_1(t)/(V\text{-}b_1')$.

$$P(t) = \frac{E(t)}{V-b'} = \frac{m_1 R_1' T_1(t) + m_2 R_2' T_2(t)}{V-(b_1' + b_2')} = P_1(t) + P_2(t) \quad (5)$$

This result can be explained by Dalton's law of partial pressure, which states that in a mixture of non-reacting gases in the same system, the total pressure exerted is equal to the sum of the partial pressures of the individual gases. The suggested model can intuitively and simply explain the energy release performance of mixed energetic materials through the law of energy conservation, or Dalton's law of partial pressure. Also, because the model estimates the performance of mixed energetic materials from the sum of the performance of each energetic material, it has the advantage of being able to independently analyze the effect of each energetic material on the overall performance.

Although the model has these advantages, there are several points to be confirmed for application to the mixed energetic materials. Because the model has the assumption that there is no interaction between the component gases, it is necessary to check this point. In addition, when mixed energetic materials combust, there is a short time delay until the secondary energetic material combusts and the primary energetic material combusts. Thus, it is necessary to analyze the influence of the time delay on the performance of mixed energetic materials. These points will be confirmed through the comparison with experiments in the results section. It will also be validated whether the model predicts the performance of each energetic material properly, through the comparison with experiments.

2-4. Thermal diffusivity of molten oxidizer layer

When the energetic material receives heat above a certain ignition temperature, the oxidizer begins to melt, and forms a thin molten oxidizer layer around the fuel. In this case, the thermal diffusivity and the thickness of the molten oxidizer layer play an important role in determining the energy generation rate. However, when the energetic material combusts, the temperature generated inside the bomb is over 1,000 K, and this makes it difficult to determine the value of thermal diffusivity of the molten oxidizer layer. Since the thermal diffusivity is affected by temperature, thermal diffusivity values at high temperatures should be used in the model. The literature referred to a thermal diffusivity value of the $KClO_x$ molten oxidizer layer of 1.8×10^{-7} m^2/s [11]. However, no value of the thermal diffusivity of the KNO_3 molten oxidizer layer at high temperature is available. Therefore, the thermal diffusivity of the KNO_3 molten oxidizer layer was calculated using thermal conductivity plots at high temperatures.

Fig. 2(a) is a graphical representation of the KNO_3 thermal conductivity values according to the temperatures given in the literature [14]. The black dot represents the thermal conductivity corresponding to the temperature written in the document, while the red solid line represents the fitted line based on the data. The thermal diffusivity can be calculated by dividing the thermal conductivity by the density and specific heat. Although the actual density and specific heat vary with temperature, it is assumed that the density and specific heat of the liquid state do not change greatly depending on the temperature, unlike the gas state. Fig. 2(b) shows the thermal diffusivity of the KNO_3 molten oxidizer layer, using the fitting line and ρ: 2,109 kg/m^3, C_p: 940.23 J/(kgK). However, the actual temperature at which the oxidizing agent, KNO_3, can form a molten oxidant layer around the fuel is from (600 to 810) K

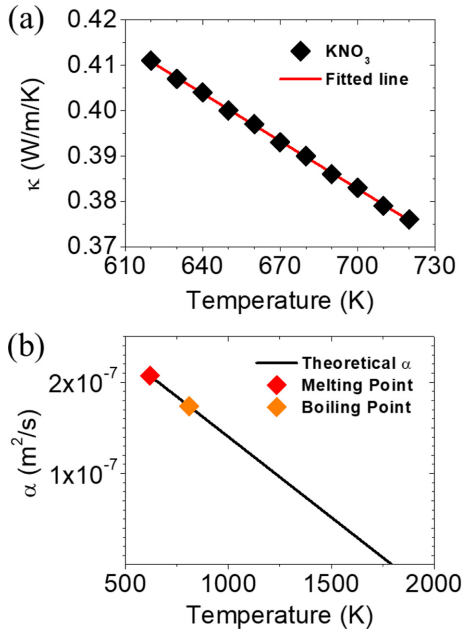

Fig. 2. (a) Thermal conductivity (κ), and (b) diffusivity (α) plot of the molten KNO_3 oxidizer layer according to temperature change.

Table 2. Parameter values of energetic materials used for model prediction

Parameter	Value
$C_{v.ZPP}$	241.7 J/(kgK) [15]
$C_{v.THPP}$	829.3 J(kgK) [16]
$C_{v.BKNO3}$	951.7 J(kgK) [17]
b	0.001 m^3/kg [13, 18]
$x_{.KClO4}$	9 x 10^{-6} m
$x_{.KNO3}$	2.2 x 10^{-5} m
$\alpha_{1.KClO4}$	1.8 x 10^{-7} m^2/s [11]
$\alpha_{1.KNO3}$	1.9 x 10^{-7} m^2/s
z	8.6 x 10^{-3} m
α_2	4 x 10^{-2} m^2/s

(the melting point of KNO_3, to the vaporization point of KNO_2), and the thermal diffusivity value of the KNO_x molten oxidizer layer can be (2.07×10^{-7} to 1.73×10^{-7}) m^2/s, respectively. Therefore, the average value of 1.9×10^{-7} m^2/s is adopted as the thermal diffusivity of the KNO_3 molten oxidizer layer in this study.

Table 2 shows the parameter values of energy materials and closed bombs used in the model to predict energy release performance for three types of energy materials, including ZPP, THPP, and $BKNO_3$. The specific heat of each energetic material (C_v) was obtained by subtracting the ideal gas constant from the values mentioned in the reference [15-17]. The co-volume value b uses the average of the values in the reference [13,18]. The values of oxidizer molten layer thickness (x) were estimated from the calculation formula in the reference [11]. The thermal diffusivity of closed bomb (α_2) was defined as an effective thermal diffusivity that is lumped by additional thermal mechanisms such as leaking and radiation that occur in experiments as well as conduction.

3. Results and Discussion

3-1. Parametric Analysis

The purpose of the closed bomb test is to estimate the pressure change, especially for maximum pressure, of energetic material for the desired application. The key factors affecting the pressure distribution are the energy contents, energy generation rate, and energy loss rate. By analyzing the parameters, it is possible to confirm which parameter has a significant effect on each factor, and how these factors determine the pressure gradient, namely, the performance. The reaction temperature indicates the energy contents of the energetic material. The characteristic time scales t_1 and t_2 indicate the energy generation rate and the energy loss rate, respectively. As a result, it would be possible to obtain insight into how these factors determine the pressure distribution when the energetic material combusts in the closed bomb. Therefore, the effects of parameters, such as the reaction temperature and the characteristic time scales t_1 and t_2 on the performance of the model under all the same conditions, except the target parameter, were analyzed. For the following parametric analyses, the reference case (195 mg of ZPP combusts in a 10 cc) is shown as a black line in the following Figs. 3-5, which was matched with experimental data.

3-1-1. Effects of reaction temperature

The reaction temperature, which can be simply calculated by using the following Modified Dulong-Petit law in Eq. (6), represents the highest temperature in a reaction completion zone [11]. It also indicates the energy contents of the energetic material.

$$T_r = T_0 + \frac{1}{9R} \times \frac{\Delta H}{N} \tag{6}$$

Because the reaction temperature is estimated by the chemical composition and heat of reaction, the model is capable of considering various energetic materials with different compositions. Table 3 shows the reaction temperature values calculated according to the thermodynamic information of the three types of energetic materials ZPP [11], THPP, and $BKNO_3$, and the temperature is higher in the order of ZPP > THPP > $BKNO_3$. Each reaction temperature value was calculated by using the reference value or calculating the enthalpy of formation data from the NIST chemistry webbook website [19] and by Eq. (6). Fig. 3 shows the comparison of the energy release performance according to the reaction temperature of these energetic materials. Practically, if the energetic material is changed, other parameters must be changed as well. However, all parameters, except the reaction temperature, were fixed to observe the effect of reaction temperature on the performance under the combustion of

Table 3. Reaction temperature of three types of energetic material calculated by dulong-petit law

Material	ΔH (kJ/mol)	N	T_r (K)
ZPP	2198.3	8	3970
THPP	1601.6	12	2082
$BKNO_3$	1554.8	14	1782

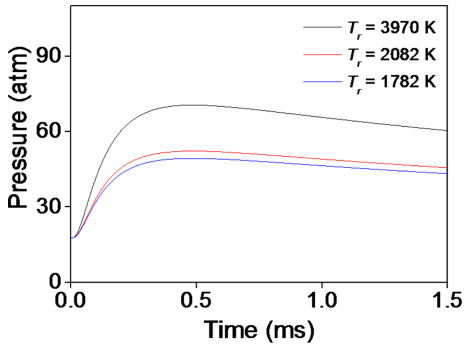

Fig. 3. Comparison of the energy release performance according to the reaction temperature, T_r. The characteristic time scale for energy generation and loss rate t_1 = 0.45 ms and t_2 = 1.85 ms, respectively.

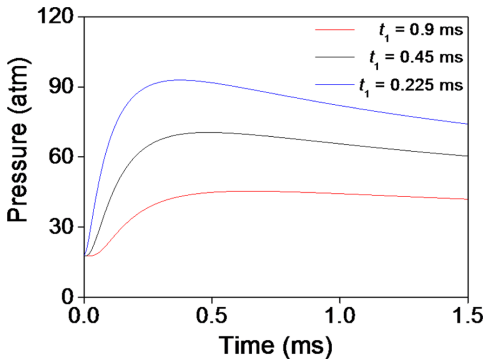

Fig. 4. Comparison of the energy release performance according to the change of the characteristic time scale for energy generation rate t_1. The characteristic time scale for energy loss rate t_2 = 1.85 ms.

the reference case (195 mg of ZPP combusts in a 10 cc bomb). Unless otherwise mentioned, all following parametric analyses will assume that all other conditions are fixed, while only the target parameter is changed under this reference condition. Under the same conditions except reaction temperature, the higher the reaction temperature, the higher the performance. This is because the reaction temperature indicates how much energy the energetic material contains, and can release. Therefore, the greater the energy of the energetic material, the higher the reaction temperature is. In the case of three energetic materials, ZPP has the highest energy content, while THPP and $BKNO_3$ have relatively low energy content. The current reaction temperature is calculated by a simple equation, but more precise value can be applied by using molecular dynamics or thermodynamic calculations, or experiments.

In addition, as time passes, energetic material can be denatured, that is aged, due to the penetration of moisture or oxygen. This can reduce the energy emitted from the energetic material, and as a result, the performance of the energetic material could be reduced. This is the one of the important issues to predict the lifetime of the energetic material. If the contained energy of the energetic material is reduced due to aging, the heat of reaction would reduce as well. Thus, using the reaction temperature, which is calculated by the heat of reaction, the performance change of energetic material could be predicted. In other words, the change of heat of reaction is measured by experiment or thermodynamic calculation, the reaction temperature of aged energetic material could be calculated, and the lifetime of the aged energetic material could be estimated by using the suggested model.

3-1-2. Effects of the characteristic time scale for energy generation

The thermal diffusivity and thickness of the molten oxidizer layer can be analyzed with one unified parameter the characteristic time scale $t_1 = x^2/\alpha_1$. In order for the energetic material to release energy, the fuel must combine with free oxygen atoms generated from the oxidizer to form fuel-dioxide, which is an exothermic reaction. Because the formation of the fuel-oxide is a rate-determining step of the entire reaction, and is an endothermic reaction, the fuel receives energy from the surrounding through the molten oxidizer layer, and combines with oxygen atom. In this case, the thermal diffusivity and thickness of the molten oxidizer layer determine how quickly the surrounding energy can reach the fuel. Therefore, the time scale t_1 indicates the time it takes for the surrounding energy to reach the fuel through the molten oxidizer layer. That is, the larger the thermal diffusivity and the thinner the thickness, the faster the energy reaches the fuel, because the characteristic time scale t_1 is reduced. Therefore, as the thermal diffusivity increases and the thickness becomes thinner, the energy can be transferred to the fuel more quickly, and the rate of formation of fuel-oxide increases, which allows the energetic material to release more energy before the energy loss progresses, so that the maximum pressure is increased as shown in Fig. 4.

3-1-3. Effects of the characteristic time scale for energy loss

When the energetic material combusts, energy is accumulated inside the bomb, and the energy is transferred from the inside to the outside through the bomb wall, that is, energy loss occurs. In the energy loss term, $t_2 = z^2/\alpha_2$ is a characteristic time scale that indicates how fast the energy loss proceeds. The thicker the thickness and the smaller the thermal diffusivity, the longer the time it takes for energy loss to start, while the energy generation rate is constant. Thus, the system can accumulate more energy, which results in a slower rate of reaching the maximum pressure, and an increase in the magnitude of the maximum pressure as shown in Fig. 5. Thus, even if the same energetic material is used, the maximum pressure is affected by the conditions of the bomb. Therefore, it is important to consider the energy loss and properties of the bomb in CBT modelling. Also, it is possible to predict the energy release performance and select a suitable bomb before the experiment by using the model, and it can help to minimize the number of experiments. In order to apply these theoretical results to actual applications, Section B will validate the pressure distribution in the actual combustion of mixed energetic materials.

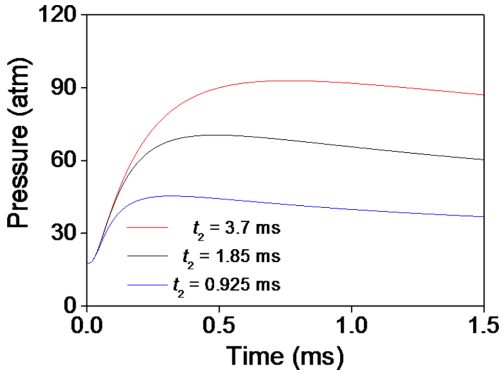

Fig. 5. Comparison of the energy release performance according to the change of the characteristic time scale for energy loss rate t_2. The characteristic time scale for energy generation rate t_1 = 0.45 ms.

3-2. Validation of mixed energetic materials energy release model

For model validation of the energy release of mixed energetic materials, the CBT result data and the predicted pressure change graphs were compared with the model. Experiments were carried out by changing the amount of one energetic material, while the amount of the other energetic material was fixed. In order to improve the reliability of the test results, all the experiments were performed 10 times, and the average of the results with the most frequent tendencies among them was used as the representative data, and the representative data were compared with the model prediction. Through the comparison with the experiment, it is possible to confirm the reliability of the model, and to analyze the effect of each energetic material independently.

3-2-1. Time delay analysis for the mixed energetic materials combustion

As mentioned above, ZPP is used as a secondary energetic material to help the combustion of primary energetic material, such as THPP or $BKNO_3$, because of its high reaction rate and easy ignition characteristics. When the mixed energetic materials combust in the closed system, the ZPP first starts to combust and the emitted energy from ZPP helps the combustion of THPP or $BKNO_3$. In other words, after the start of the secondary energetic material combustion, a time delay occurs until the combustion of the primary energetic material. Therefore, considering that the time delay between the secondary and primary energetic material in the combustion of the mixed energetic materials can be an important factor, it is necessary to analyze the effect of this time delay on the energy release performance of the mixed energetic materials.

In order to consider the time delay, it is important to consider the temperature where each energetic material begins to react, which is the ignition temperature (T_{ig}). Ignition temperatures of the energetic materials are about (658, 773, and 823) K for ZPP [10], THPP [20], and $BKNO_3$ [21], respectively. Therefore, the time where the combustion of THPP and $BKNO_3$ starts can be calculated by the temperature change when ZPP combusts. Fig. 6 shows the overall and the partial temperature change when the ZPP energetic material combusts, calculated by an energy generation term of the suggested model. The blue and red points represent the ignition temperature of $BKNO_3$ and THPP, respectively. It can be confirmed that the temperature is (773.3 and 825.8) K at (0.1 and 0.106) ms, respectively. Thus, it can be assumed that the combustion of the primary energetic material starts at about 0.1 ms, and the time delay is approximately 0.1 ms. Therefore, by adding the time delay to the pressure change of the primary energetic material in Eq. (1), the energy release performance of the mixed energetic materials can be compared when the time delay is considered or not.

Fig. 7 shows the performance of mixed energetic materials when the delay is considered or not. Fig. 7(a) shows that for the ZPP and THPP mixed energetic materials, when the time delay is considered and when not considered, the maximum pressure is (84.2 and 84.4) atm, respectively (0.2% difference between the two cases). Also, Fig. 7(b) shows the cases for ZPP and $BKNO_3$ when the time delay is considered or not, and the maximum pressure is (51.9 and 51.2) atm, respectively (1.3%). Therefore, when the time delay is considered using the suggested model, it can be seen that the time delay from the combustion of the secondary energetic material to the start of combustion of the primary energetic material does not significantly affect the performance of the mixed energetic materials. Based on these results, it is possible to calculate the pressure of the mixed energetic materials by adding the pressure of each energetic material without considering the time delay, and it shows that

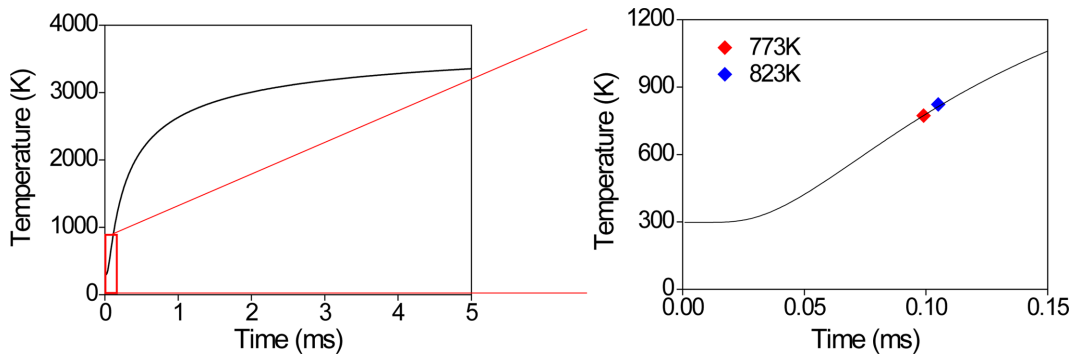

Fig. 6. Temperature change of ZPP combustion obtained from the energy generation term of the model.

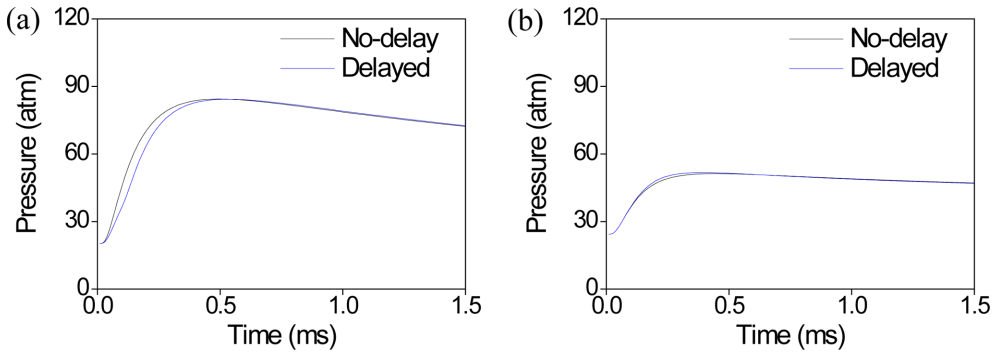

Fig. 7. Comparison of the energy release performance of the mixed energetic materials of (a) ZPP 55 mg & THPP 160 mg, and (b) ZPP 60 mg & $BKNO_3$ 160 mg, when the time delay was considered (blue line), or not (black line).

there is no significant problem for the result and the convenience of calculation.

3-2-2. ZPP & THPP mixed energetic materials modelling

To validate the performance of the energy release model for mixed energetic materials, we first tried the mixture of ZPP and THPP. In this case, it was assumed that the combustion of both energetic materials occurs simultaneously, without time delay, as a result of Fig. 7. For the cases of model prediction, all parameters, except the amounts of ZPP and THPP energetic materials, were fixed for accurate comparison. Fig. 8 shows the pressure change of ZPP and THPP mixed energetic materials in 10 cc bomb according to the amount of energetic materials. Fig. 8(a) shows the comparison graph when ZPP 55 mg and THPP 160 mg combust. In this case, the difference of maximum pressure between experimental result and model prediction is 1.5%. Fig. 8(b) shows the comparison when increasing the amount of ZPP only, and the difference is 1.6%. Fig. 8(c) shows the comparison when increasing the amount of THPP only, and the difference is 0.7%. For the three cases with changing amounts of energetic material, even though the predictions are closed-form analytical solution, the differences of the maximum pressure are less than 2%, indicating the theoretical predictions and the corresponding experimental results show quite good agreement according to the amount of energetic material.

In practice, when using an igniter, the pressure required for the system is adjusted by changing the amount of energetic material charged to the igniter. Therefore, it is very important to predict the performance depending on the amount of energetic material in the same system. Fig. 8 validates that the prediction of the model fits the experimental data well when the amount of one energetic material species is fixed, and the amount of another energetic material species is changed, even though all parameters are fixed. In other words, the model can explain both the performance of each energetic material, and the performance of the mixed energetic materials; and it also means that the assumption that calculates the performance of the mixed energetic materials by adding the performance of each is valid.

The pressure gradient shape of the ZPP and THPP mixed energetic

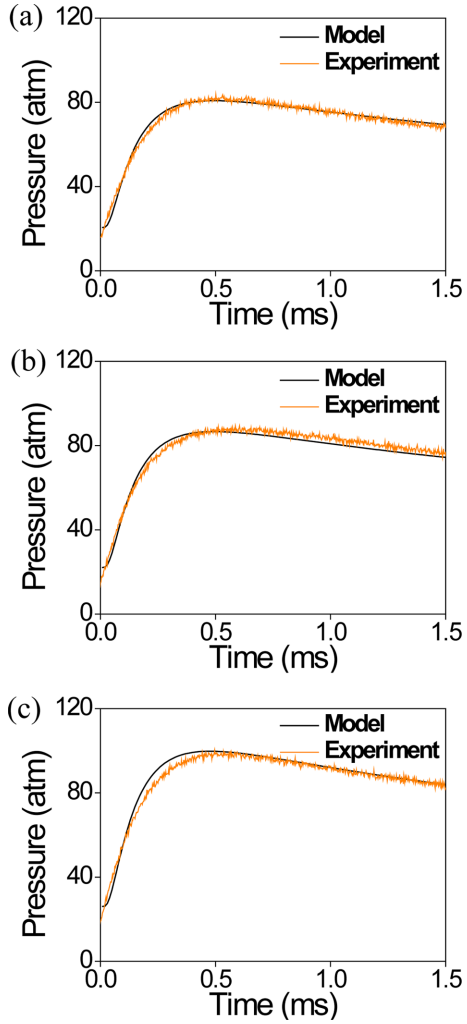

Fig. 8. Comparison of the experimental results (orange line) and model predictions (black line) for ZPP & THPP mixed energetic materials combustion according to the amount of energetic material. (a) ZPP 55 mg & THPP 160 mg (83.7 atm, the maximum pressure of experimental data), (b) ZPP 65 mg & THPP 160 mg (89.3 atm), and (c) ZPP 65 mg & THPP 182 mg (99.9 atm).

materials is similar to the shape of the ZPP single energetic material in Fig. 4, because of the same oxidizer. Because the ZPP is composed of Zr fuel and $KClO_4$ oxidizer, and the THPP is composed of TiH_2

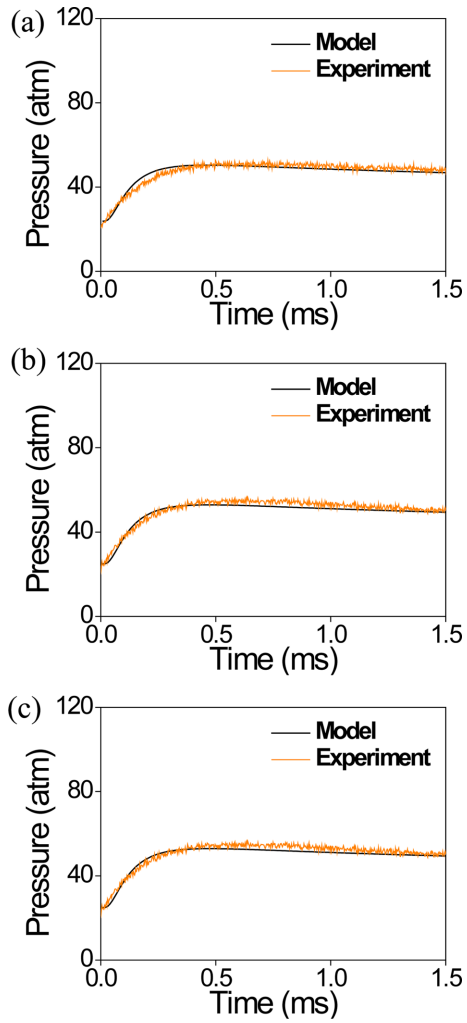

Fig. 9. Comparison of the experimental results (orange line) and model predictions (black line) for ZPP & $BKNO_3$ mixed energetic materials combustion according to the amount of energetic material. (a) ZPP 60 mg & $BKNO_3$ 160 mg (52.8 atm, the maximum pressure of the experimental result), (b) ZPP 70 mg & $BKNO_3$ 160 mg (54.1 atm), and (c) ZPP 70 mg & $BKNO_3$ 184 mg (57.4 atm).

fuel and $KClO_4$ oxidizer, the same molten oxidizer layer characteristic value can be applied to both energetic materials.

3-2-3. ZPP & $BKNO_3$ mixed energetic materials modelling

The validation of model prediction for ZPP and $BKNO_3$ mixed energetic materials was also implemented using the same method applied to the mixed energetic materials of ZPP and THPP. Fig. 9 shows the pressure change of ZPP and $BKNO_3$ in the 10 cc bomb. Fig. 9(a) shows the comparison with ZPP 60 mg and $BKNO_3$ 160 mg. Here, the difference of maximum pressure between experimental result and model prediction is 2.1%. Fig. 9(b) shows the comparison when increasing the amount of ZPP only, and the difference is 2.2%. Fig. 9(c) shows the result when increasing the amount of $BKNO_3$ only, and the difference is 1.9%. For the three cases, the differences of the maximum pressure are about 2%, which confirm the model well predicted the performance according to the amount of energetic material.

The graph shape of the ZPP and $BKNO_3$ mixed energetic materials are completely different from those of the ZPP and THPP mixed energetic materials. For the ZPP and $BKNO_3$, it can be confirmed that the pressure increases gently, and energy loss hardly occurs until 1.5 seconds. Furthermore, it can be seen that the maximum pressure of ZPP and $BKNO_3$ is significantly lower than the maximum pressure of ZPP and THPP, although similar amounts of energetic material are used. Because the molten oxidizer layer of KNO_3 (2.2×10^{-5} m) is thicker than the molten oxidizer layer of $KClO_4$ (0.9×10^{-5} m), the energy generation rate of $BKNO_3$ is slower than that of ZPP or THPP. Therefore, ZPP and $BKNO_3$ generate less energy than ZPP and THPP before energy loss occurs, and the energy generation rate is balanced by the energy loss rate. In other words, although $BKNO_3$ and THPP have similar reaction temperature, the difference in the characteristics of the molten oxidizer layers of $BKNO_3$ and THPP affects the low pressure of ZPP and $BKNO_3$ combustion. Thus, using the model gives insight into the combustion characteristics of the energetic material, and can be used to interpret the experimental results.

As with the case of ZPP and THPP, the theoretical model well predicted the performance according to the amount of energetic materials for the case of ZPP and $BKNO_3$. Even though the model is a closed-form analytical solution, it can be seen that the model explains the energy release performance of the mixed energetic materials well in various conditions, like change of the amount of each energetic material. This is because the model considers the characteristics that vary depending on the type of energetic material, such as reaction temperature and molten oxidizer layer characteristics. These characteristics allow the model to precisely estimate the performance, especially the maximum pressure, through various factors, such as energy contents, energy generation rate, and energy loss rate. Furthermore, it was confirmed that the suggested model can independently analyze the performance of each energetic material of the mixed energetic materials through the simple approach of adding the energy performance of each energetic material. In this case, because the time delay of the mixed energetic materials is very short, and doesn't significantly influence the performance, it is possible to estimate the performance of mixed energetic materials conveniently without considering the time delay. Therefore, the energy release performance for various types of single or mixed energetic material combustion could be estimated using the suggested single general model.

4. Conclusion

Based on the model that describes the combustion performance of single energetic material, the mixed energetic materials energy release modelling was conducted. The energy release performance of the mixed energetic materials was easily explained by the

straightforward assumption of calculating the performance of the mixed energetic materials by adding the performance of each energetic material without time delay. Through the model, the effects of the parameters on the energetic material performance were systematically analyzed. The parametric analysis confirmed how the pressure gradient is determined in the combustion of energetic material in closed bomb through the factors such as energy contents, energy generation rate, and energy loss rate. In order to apply the theoretical results to actual applications, the experimental results of the mixed energetic materials (ZPP/THPP and ZPP/$BKNO_3$) were compared with the model predictions, under the condition that the amount and type of energetic material were changed. The model showed fairly good agreement, confirming the reliability of the model. From the theoretical model, it was possible to gain insight into the energy release performance of energetic material in closed bomb, considering the characteristics of combustion, and to utilize the interpretation of the experimental results. These results could help to select the suitable energetic material and bomb for specific application. Because the suggested model is a closed-form analytical solution, it could easily be applied to various applications. Finally, we hope this model can be used to analyze the aging of energetic material. It could be possible to predict the lifetime of aged energetic material, by quantitatively estimating the performance change of aged energetic material with reaction temperature.

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Nomenclature

A : Outer surface area of the bomb [m^2]
b : Specific co-volume [m^3/kg]
b' : Co-volume, the volume occupied by gas molecules produced from the energetic material, $b' = mb$ [m^3]
C_v : Specific heat at constant volume [kcal/kg/K]
E : Total energy [J]
$erfc$: Complementary error function
h : Heat transfer coefficient [$W/m^2/K$]
m : Mass of energetic material [kg]
N : The total number of atoms in the reaction formula
n : The number of moles of gases [mol]
P : Pressure [Pa]
R : Reaction rate [m/s]
R : Gas constant [J/K/mol]
R' : Specific gas constant [J/kg/K/mol]
T : Temperature [K]
T_0 : Initial temperature, 298 K
T_a : Temperature at adiabatic condition [K]
T_{ig} : Ignition temperature [K]
T_s : The outer surface temperature of a closed bomb [K]
T_r : Reaction temperature of the energetic material [K]
t : Time [s]
t_1 : Characteristic time scale for energy loss rate, x^2/α_1 [s]
t_2 : Characteristic time scale for energy generation rate, z^2/α_2, [s]
V : Total volume of the system [m^3]
v : Specific volume, $v=V/m$ [m^3/kg]
x : Thickness of oxidizer layer [m]
z : Thickness of a closed bomb [m]
α_1 : Thermal diffusivity of the molten oxidizer layer [m/s^2]
α_2 : Thermal diffusivity of a closed bomb [m/s^2]
ΔH : Heat of reaction [kJ/mol]

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