A study on the ignition
of boron / potassium nitrate mixture

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Abstract

The ignition properties of boron / potassium nitrate (B / KNO_3) have been investigated using a carbon dioxide (CO_2) laser. The ignition delay time and surface temperature of a B / KNO_3 sample were measured. The effects of the purity of boron and the particle size of potassium nitrate on the ignition delay time are discussed in the paper. In addition, a theoretical model was presented to investigate the ignition behavior of B / KNO_3. A one-dimensional heat equation with an Arrhenius type chemical reaction source was solved using a physical splitting technique. The surface temperature history of the sample was calculated and compared with that of experiments.

Keywords: Ignition, Boron, Potassium nitrate, CO_2 laser, Numerical calculation

1. Introduction

Boron / potassium nitrate (B / KNO_3) is extensively used in the pyrotechnic field because of its good ignition characteristics. For example, it is widely used in automobile airbag gas generators as an ignition charge to ignite gas generators.

A laser is one type of energy source employed for fundamental studies of the ignition behavior of pyrotechnics because it offers the advantages of a precise control of heating time, energy flux and spot size on the surface of a sample. In this work, a carbon dioxide (CO_2) laser is used as an ignition source to ignite a B / KNO_3 mixture. Ignition delay time as a function of laser heat flux was measured. The surface temperature of sample was also measured using a Chromel- Alumel thermocouple. The effects of the purity of boron and the particle size of potassium nitrate on ignition delay time are discussed.

A simple theoretical model was used to calculate the surface temperature of B / KNO_3 heated by a laser beam. A one-dimensional heat equation without a chemical reaction source term is solved analytically. However, the equation with an Arrhenius type chemical reaction source complicates the solution of this type of problem. A physical splitting technique proposed by Yanneko[1] was used to numerically solve the equation. The results of numerical calculations are compared with that of experiments.

2. Experimental
2.1 Samples

The samples of four kinds of B / KNO_3 mixtures were tested in this work. The purity of boron and the particle diameter of potassium nitrate utilized in these mixtures are listed in Table 1. Impurities included in the boron were magnesium and small amounts of anhydrous boron oxide, etc. The average particle diameter of the boron was less than 1.2 μm. The purity of the potassium nitrate utilized as an oxidizer was above 98 %.

A B / KNO_3 mixture with a weight ratio of 25 / 75 was prepared using an ordinary ball-mill mixer.

The B / KNO_3 mixture was pressed into a cylinder pellet measuring 2 mm in length by 4 mm in diameter, using a hydraulic press with about 30 MPa of pressure. The density of the sample utilized in the experiments was about 1800 kg·m⁻³.

Table 1 Samples of B / KNO_3 mixtures.

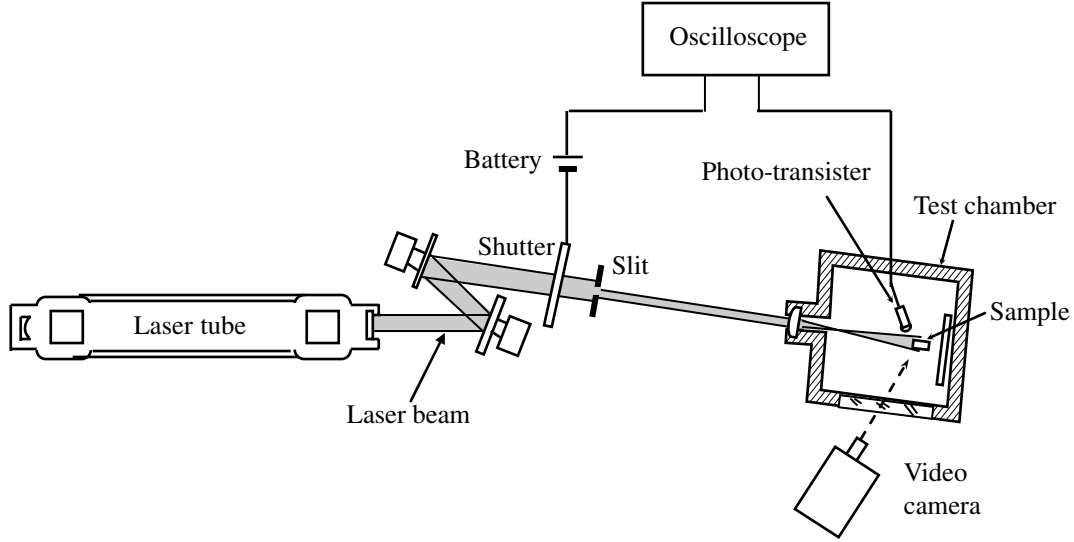| Name of sample	Purity of boron	Average particle diameter of KNO_3
G I	96 - 98 %	60 m
G II	90 - 92 %	60 m
G III	86 - 88 %	60 m
K200	90 - 92 %	200 m

Fig. 1 Schematic diagram of experimental setup.

2.2 Ignition device using CO_2 laser

A schematic diagram of the experimental setup used in this work is shown in Fig. 1. The experimental setup is located at the Institute of Space and Astronautical Science, Japan, has been discussed in detail by Takeo Saito et al.[2] and only a brief overview will be given here.

A CO_2 laser (100 w, 10.6 μm) was used for all of the ignition experiments. A sample was centered in the test chamber and exposed to the uniform laser beam. The diameter of the laser beam was slightly larger than that of the sample.

The ignition was monitored with a phototransistor, which senses light emissions from the sample. The output signal was recorded by a digital oscilloscope that was triggered by a synchronization signal from the laser at the onset of laser heating. For each test, the time difference between the synchronization signal from the laser at the onset of laser heating and light emission from the sample is recorded as the ignition delay. A video camera was also employed to record the ignition phenomenon. The surface temperature of the sample was measured by a Chromel-Alumel thermocouple (d = 30 μm), which was attached to the surface of the sample. The temperature measurement method was previously described in detail by Takeo Saito et al.[2] and Michiko Harayama et al.[3].

3. Mathematical model

A mathematical model of solid heating with laser heat flux is presented.

To simplify the governing equations, the following assumptions were made.
(1) There is no reflection of the laser beam on sample surface. The heat flux is constant and is absorbed totally on the sample surface.
(2) The length of sample is greater than the thickness heated from surface into the sample before ignition.
(3) Thermal properties (thermal conductivity and thermal diffusivity) are constant.
(4) There is no phase change.

Therefore, in the case of a semi-infinite boundary in which no chemical reaction occurs, the heat transport can be expressed by one-dimensional equation as follows.

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} \qquad x > 0 \tag{1}$$

with initial condition ($t = 0$)

$$T(x,0) = T_0 \tag{2}$$

where T_0 is the initial temperature, with the boundary condition ($x = 0$)

$$q = -\lambda \frac{\partial T}{\partial x} \tag{3}$$

where $T(x, t)$ is the instantaneous temperature; q is the heat flux to sample surface. κ is the thermal diffusivity that is defined as

$$\kappa \equiv \frac{\lambda}{\rho c} \tag{4}$$

where λ is the thermal conductivity; ρ is the density; c is the specific heat.

Laplace transforms are used to solve equation (1), and the following analytical solution is obtained.

$$T = \frac{2q}{\sqrt{\rho c \lambda}} \sqrt{\frac{t}{\pi}} \left[e^{-\theta^2} - \sqrt{\pi} \cdot \theta \cdot erfc(\theta) \right] + T_0 \tag{5}$$

where θ is expressed by the following formula.

$$\theta = \frac{x}{2\sqrt{\kappa t}} \qquad x > 0 \tag{6}$$

and *erfc* is the complementary error function that is

defined as

$$erfc(\theta) = \frac{2}{\sqrt{\pi}} \int_{\theta}^{\infty} e^{-t^2} dt \tag{7}$$

which has a special value $erfc(0)$, when $\theta = 0$.

At the sample surface ($x = 0$), the above solution gives a relation between the surface temperature $T(0, t)$ and the heating time t.

$$T(0,t) = \frac{2q}{\sqrt{\rho c \lambda}} \sqrt{\frac{t}{\pi}} + T_0 \tag{8}$$

When the surface temperature reaches an ignition temperature, the sample is ignited.

Satisfying formula (8) means that the sample is heated physically, because formula (8) is drawn on the assumption that there is no chemical reaction occurring. Actually, when energetic material such as B / KNO$_3$ mixture are heated by heat flux, the material is not only heated physically but also heated by a chemical reaction in the heated domain. In this case, we also assume that an Arrhenius type chemical reaction occurs during ignition. Therefore, the following general expression for heat transport with chemical reaction is used instead of equation (1).

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} + \frac{Q}{c} \cdot A \cdot e^{-E/RT} \quad x > 0 \tag{9}$$

Where, Q is the heat of reaction, A is the pre-exponential factor, E is the activation energy and R is the gas constant.

Equation (9) includes an Arrhenius type chemical reaction source term, which makes solution more difficult. To solve equation (9) numerically with boundary condition (3), a physical splitting technique proposed by Yanneko[1] was used in this work. In each small time integration step Δt, equation (9) can be integrated with two steps called a reaction step and a diffusion step. Proper numerical methods can be used for each fractional step individually.
(1) Reaction step (denoted by operator L_R):

$$\frac{dT}{dt} = \frac{Q}{c} \cdot A \cdot e^{-E/RT} \tag{10}$$

This is an ordinary differential equation and the time integration process can be performed using a fourth order accuracy Runge-Kutta method.
(2) Diffusion step (denoted by operator L_D):

$$\frac{\partial \bar{T}}{\partial t} = \kappa \frac{\partial^2 \bar{T}}{\partial x^2} \tag{11}$$

where $\bar{T}$ is the calculated value from the reaction step.

The partial differential equation can be integrated using a second order accuracy Crank-Nicolson implicit method.

Therefore, the integration of equation (9) within each small step Δt can be presented by the following expression.

$$T^{n+1} = L_D(\Delta t) L_R(\Delta t) T^n \tag{12}$$

where T^n, T^{n+1} are the temperatures before and after a small time integration step Δt, respectively.

To solve equation (8) and equation (9), it is necessary to obtain the material properties of B / KNO$_3$, such as ρ, c, λ, Q, A, and E. The density of B / KNO$_3$ pt utilized in the experiments is about 1800 kg·m^{-3}. Except for density ρ, there are no available data for the other parameters in the literatures. However, the typical values for these parameters for other pyrotechnic mixtures are reported by Ph. Gillard and M. Roux[4] and were employed for the various laser heat fluxes in this paper.
$c = 1000$ Jkg^{-1}K^{-1}, $\lambda = 0.14$ Wm^{-1}K^{-1}, $Q = 6.3 \times 10^6$ J kg^{-1}, $A = 10^{13}$s^{-1}, and $E = 2.15 \times 10^5$ J mol^{-1}

4. Results and discussion
4.1 Ignition characteristics

The typical measured and calculated surface temperature history of B / KNO$_3$ mixtures are shown in Fig. 2.

Both measured and calculated results show that the surface temperature increases gradually when heated by a laser beam. The exothermic reaction gradually becomes dominant after the temperature reaches above 770 K. Then, the temperature increases rapidly, and eventually an ignition event occurs at a temperature near 830K. There are no qualitative differences in ignition temperature for heat flux 16.7 J·cm^{-2}·s^{-1} and 18.8 J·cm^{-2}·s^{-1}. Figure 3 shows the DTA curve of sample G II. It can be seen that a maximum exothermic redox reaction between boron and potassium nitrate occurs at temperature of 834 K.

From equation (9) with boundary condition (3), it can be seen that the increasing rate of surface temperature, which leads in the attainment of ignition temperature, is dependent on the incident heat flux, diffusion rate of energy and chemical reaction.

Figure 2 indicates that the analytical calculated result from formula (8) is completely in agreement with that of numerical calculation using equation (9) with boundary condition (3) within a temperature range of 298 - 770 K.
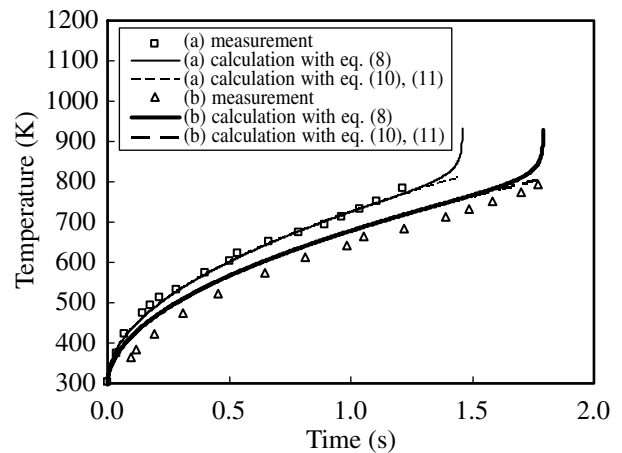

Fig. 2 Surface temperature of sample G II
(a)q=16.7 J·cm^{-2}·s^{-1}; (b)q=18.8 J·cm^{-2}·s^{-1}.
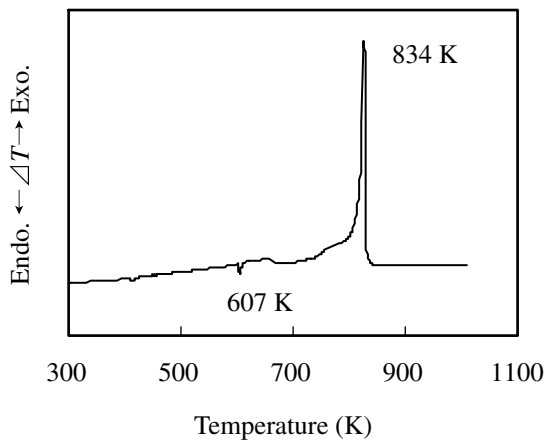
Fig. 3 DAT plot for sample G II (heating rate 10 K·min⁻¹).

Fig. 4 Temperature profiles inside of sample G II (q=18.8 J·cm⁻²·s⁻¹).

It implies that the samples undergo only a heat conduction process without chemical reaction when the temperature is less than 770 K. The chemical reaction becomes dominant and the temperature rises very rapidly when the temperature exceeds 770 K.
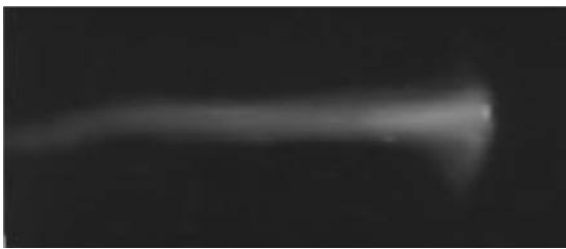
The results shown in Fig. 2 also indicate that the
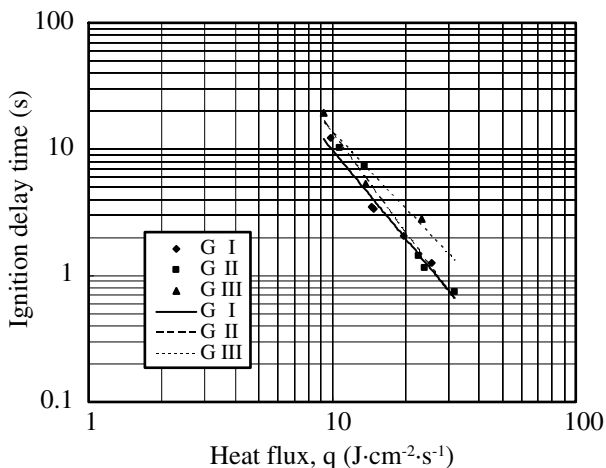

Fig. 5 Photograph of ignition phenomena.

Fig. 6 Relation between heat flux and ignition delay time for G I, G II and G III.
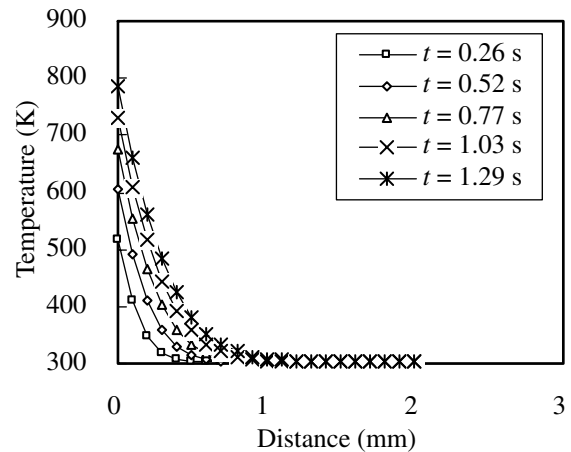
increased heat flux results in a short ignition delay because the energy on the surface of sample increases and the increasing rate of surface temperature becomes rapid.

Temperature profiles within the sample along the direction of the incident laser beam are shown in Fig. 4. It can be seen that the sample is heated only to a small depth and it appears that ignition occurs near the surface.

Figure 5 is a photograph of the ignition phenomena taken by a video camera. The first light after ignition clearly appears at the center of the laser beam on the sample surface.

4.2 Influence of boron purity

Figure 6 displays the experimental results of the ignition delay time as a function of the incident heat flux for the samples of G I, G II and G III, respectively. A linear plot of ignition delay time versus heat flux in logarithmic scale implies that the ignition delay time as a function of the incident heat flux can be expressed with an exponential equation.

As can be seen in Fig. 6, the ignition delay behaviors of G I, G II and G III exhibited the following trends: t_{ig} (G I) < t_{ig} (G II) < t_{ig} (G III). The result implies that the ignition delay time is short when the purity of boron is high. DTA plots show that the maximum exothermic peaks appear at temperatures of 824 K, 834 K and 847 K for G I, G II and G III, respectively. It also shows the same tendency that a high purity of boron results in a low ignition temperature. Impurities included in boron are magnesium and a small amount of anhydrous boron oxide. According to Conkling J. A.[5], the ignition temperature of magnesium and potassium nitrate mixture is 923 K, which is higher than that of B / KNO_3 mixture. Therefore, it is possible that the exothermic reaction becomes more dominant at low temperature as the purity of boron is high, resulting in early energy release in the heated area and short ignition delay time.
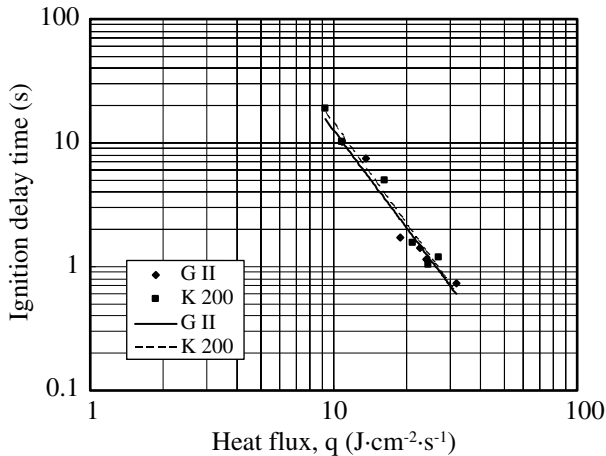
Fig. 7 Relation between heat flux and ignition delay time
for G II and K200.

4.3 Influence of KNO₃ particle size

The experimental results of the ignition delay behavior as a function of the laser heat flux for the samples of G II and K 200 are depicted in Fig. 7. The results show that the average particle diameter of potassium nitrate within 60 - 200 μm does not have a significant influence on the ignition delay time. It is possible that the potassium nitrate has already melted whether the particle size is large or not when the temperature approaches the ignition temperature, because the potassium nitrate melts at 607 K. Meanwhile, the boron has not yet melted during the ignition because the melting point of the boron is very high (2350 K). Therefore, it is believed that an exothermic redox reaction on the surface of the boron particles is governing the ignition event. However, properties for particle diameters beyond 60 - 200 μm has not yet been acquired.

5. Conclusions

The CO_2 laser ignition behavior of B / KNO_3 mixtures has been investigated by experimentation and theoretical calculations, and the following conclusions were obtained in this work.

(1) Both measured and calculated results indicate that B / KNO_3 undergoes only a physical heating when the temperature is below 770 K in a heated domain and the chemical heat becomes dominant at 770 K and above.

(2) The experimental results show that the ignition delay time as a function of the incident heat flux can be expressed with an exponential equation.

(3) B / KNO_3 mixture exhibits a tendency towards short ignition delay time when the purity of boron is high.

(4) The ignition delay time is less influenced by the particle size of potassium nitrate within average particle diameters between 60 - 200 μm.

Acknowledgements

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