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EVALUATION OF EFFECTIVE THERMAL CONDUCTIVITY OF FIREWORKS COMPOSITIONS

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Effective thermal conductivity of fireworks raw materials and their mixture have been measured by the temperature modulated DSC and the hot wire method, in order to predict spontaneous ignition properties precisely. As a result, an excellent linear correlation has been obtained between the density and the λ_e by the TMDSC method. Moreover, the low-density data by the hot wire method lie on the extrapolated point of the linear correlation. Thus, the λ_e within the ordinary limit of fireworks composition can be measured by the TMDSC method. Krupiczka's estimation method shows a good agreement with the experimental values.

Keywords: *effective thermal conductivity, fireworks, TMDSC*

Introduction

Fireworks mixtures composed of oxidizers and combustibles are highly reactive and require careful handling in their manufacture and use. Many accidents have happened so far in Japan, and spontaneous ignition accounts for 15% of the causes [1]. It is therefore desired to develop a proper evaluation of spontaneous ignition hazard [2–5]. Thermal conductivity is very important factor to evaluate spontaneous ignition hazard [6]. However, the thermal conductivity data of fireworks compositions are not obtained experimentally, because the compositions are very sensitive to heat, friction and shock.

In this study, the evaluation method of the effective thermal conductivity has been investigated from the viewpoint of safety and simplicity in order to be applied to hazardous materials such as fireworks compositions. Many methods are known as experimental methods of thermal conductivity, such as a flash method, a probe method, a hot wire method and a temperature modulated DSC method (TMDSC) and so on [7]. We have investigated a TMDSC method especially, because it needs the amount of the sample of about 200 mg.

Experimental

Fireworks raw materials tested are KNO_3, $KClO_3$, $KClO_4$ and aluminum. A fireworks mixture of $KClO_3/S/CuSO_4\cdot5H_2O$ (7:3:1 mass ratio) is also tested. The aluminum is flaky powder and its mean particle size is about 8 μm. Other materials are in the commercially available grade and have been sieved through 75 μm.

A thermal conductivity of a raw material is mainly measured by a modified TMDSC method by Marcus *et al*. [8]. TMDSC is a patented technique from TA Instruments in which the test specimen is exposed to a linear heating method which has a superimposed sinusoidal oscillation (temperature modulation), resulting in a cyclic heating profile. Deconvolution (separation) of the resultant experimental heat flow during this cyclic treatment provides not only the 'total' heat flow available from conventional DSC, but also separates that total flow into its reversing (heat capacity related) and non-reversing (kinetic) components, thereby providing unique insights into materials, including direct measurement of heat capacity. Thermal conductivity is predicted from heat capacity by using simple assumption of Marcus *et al*. [8].

TMDSC measurements were carried out on a Model 2920 (temperature modulation type differential scanning calorimeter, TA Instruments). The mass of materials measured by the TMDSC method was about 200 mg. It was first equilibrated at 303 K, and then heated up to 373 K at a constant heating rate of 1 K min^{-1} with a modulation amplitude of ±1 K and for period of 80 s. TMDSC method is more desirable than the hot wire method for explosive substances, because it can be safely measured with a small amount of sample. However, few data of explosive substances have been reported by the TMDSC method, so its reliability is not clear. Furthermore, the TMDSC method is not applied, when a substance

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cannot be formed into desirable shape by pressure and when a substance is granular and flaky.

Hot wire method (KEM, QTM-500) was also carried out for comparison. The hot wire method can be applied to granular and flaky substances, but needs a large amount of sample (50–100 g). Therefore, using both methods, we examine a relationship between λ_e and density and aim to predict λ_e with wide range density.

Three estimation methods of λ_e have been compared with the experimental methods. Kunii proposed the following equation, in order to estimate heat transfer characteristics of porous rocks and consolidated particles [9]. In Eq. (1), *F* and *S* are of fluid (air in this study) and crystalline material, respectively. ε is porosity, calculated by the Eq. (2). ϕ is obtained from a special diagram.

$$\frac{\lambda_e}{\lambda_F} = \varepsilon + \frac{1-\varepsilon}{\phi + \frac{2}{3}\frac{\lambda_F}{\lambda_S}} \tag{1}$$

Krupiczka statistically analyzed enormous observed λ_e data and obtained the following empirical equation [10].

$$\frac{\lambda_e}{\lambda_F} = \left(\frac{\lambda_F}{\lambda_S}\right)^n \tag{2}$$

where

$$n=0.280-0.757\log\varepsilon-0.057\log(\lambda_S/\lambda_F) \tag{3}$$

Schlünder proposed a simple method of not considering the porosity [11], as shown in Eq. (4).

$$\frac{\lambda_e}{\lambda_F} = \frac{2}{1-\lambda_F/\lambda_S}\left[\frac{\ln(\lambda_S/\lambda_F)}{1-\lambda_F/\lambda_S} - 1\right] \tag{4}$$

In above three methods, the thermal conductivity of the fluid (air) is the value of 300 W m^{-1} K^{-1}. Observed λ_S values of aluminum and KNO_3 are 220 and 0.9 W m^{-1} K^{-1}, respectively. The λ_S values of $KClO_3$, $KClO_4$ are not known, so we assume the value of 0.5 W m^{-1} K^{-1}.

Results and discussion

Figure 1 shows the relationship between the effective thermal conductivity obtained by the TMDSC method and the hot wire method and density for the fireworks oxidizers. Table 1 shows the comparison between experimental and estimated λ_e.

All materials measured show low effective thermal conductivities. Metal aluminum conducts heat very well and its λ_S is 237 W m^{-1} K^{-1} around 300 K. The λ_S of the aluminum fine powder obtained by the hot wire method was very low. Fine powder made of aluminum, magnesium or magnalium is Mg/Al alloy, which are widely used for fireworks composition, should be quite different from the one of massive metal and have low λ_S.

As shown in Fig. 1, excellent linear relationships exist between λ_e and the density within the measured range. Notice that the low-density data by the hot wire method lie on the extrapolated point of the linear correlation by the TMDSC method. The powder mixture in an actual fireworks composition has low density like in the hot wire method. Conversely, the high-density data by the TMDSC can be applied to hardened fireworks mixture, bound with an adhesive such as rice starch, like a star in a shell. The temperature dependency of λ_e by the TMDSC method has been low within the measured temperature range from 300 to 370 K.

Three estimation methods can reproduce the low thermal conductivities, even with aluminum powder. Schlünder's method cannot predict whether the density or porosity dependency of λ_e. Kunii's method reproduces low-density data well, but gives higher values in the region of high density. Moreover, ϕ expressed in Eq. (1) is complicated to be obtained by

Table 1 Comparison of experimental and estimated λ_e (in W m^{-1} K^{-1})

	Experimental	Estimation		
	this work	Kunii	Krupiczka	Schlünder
KNO_3	0.18 (hot wire, ρ=1.48, ε=0.30) 0.34 (TMDSC, ρ=1.85, ε=0.12)	0.25 1.07	0.22 0.61	0.16
$KClO_3$	0.16 (hot wire, ρ=1.52, ε=0.33) 0.34 (TMDSC, ρ=1.98, ε=0.13)	(0.16) (0.56)	(0.15) (0.35)	(0.13)
$KClO_4$	0.16 (hot wire, ρ=1.14, ε=0.55) 0.34 (TMDSC, ρ=1.87, ε=0.26)	(0.08) (0.23)	(0.09) (0.19)	(0.13)
Al (P2000) flaky	0.18 (hot wire, ρ=0.53, ε=0.80)	0.11	0.10	0.47

ρ in g cm^{-3}, values in the parenthesis – assuming λ_S of the substance=0.50

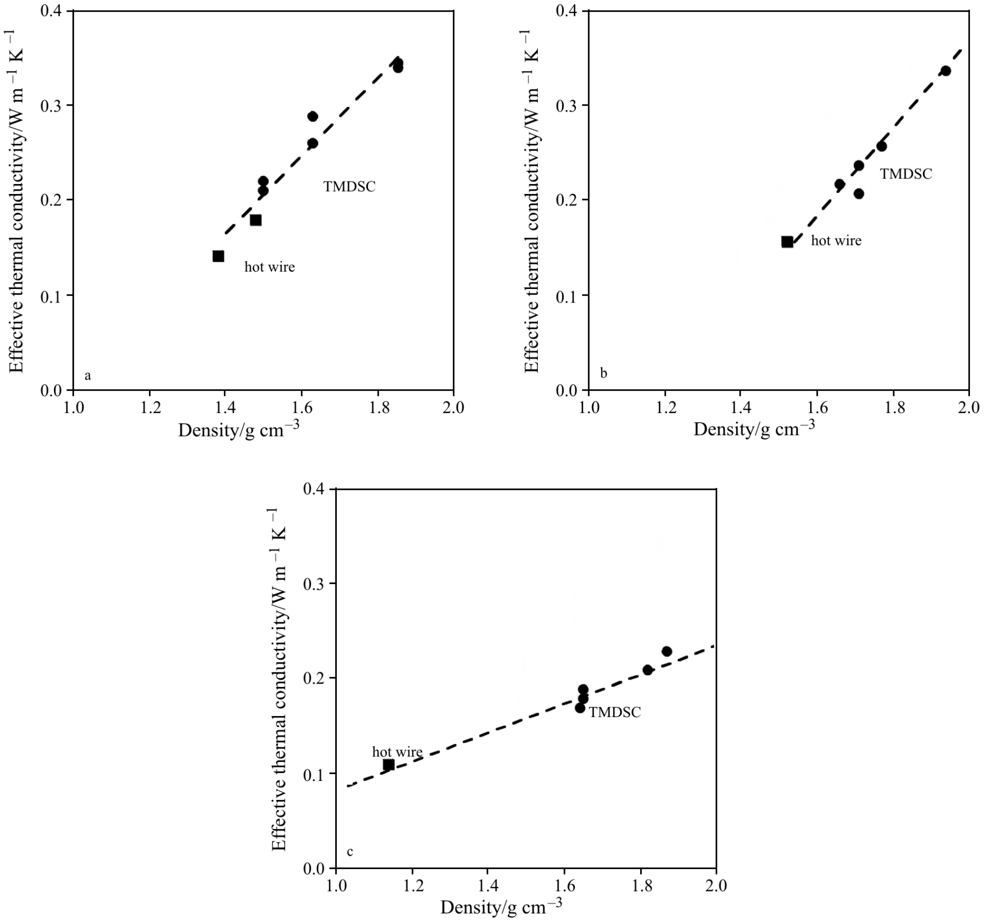

Fig. 1 Relationship between effective thermal conductivity (λ_e) and density (ρ) for oxidizers; a – KNO_3, b – $KClO_3$ and c – $KClO_4$

the special diagram. Krupiczka's method is easy to calculate and shows good agreements with the experimental values. All three methods require the λ_S value under the crystal or massive metal condition, while the available λ_S data of fireworks raw materials are few. However, we can obtain the λ_S value in the wide range of density by the TMDSC method. The following linear equations have been obtained by fitting the correlations shown in Fig. 1.

$$\lambda_e=0.41\rho-0.41 \text{ for } KNO_3 \quad (5)$$

$$\lambda_e=0.46\rho-0.55 \text{ for } KClO_3 \quad (6)$$

$$\lambda_e=0.15\rho-0.07 \text{ for } KClO_4 \quad (7)$$

Figure 2 shows a relationship between the effective thermal conductivity obtained by the TMDSC method and the hot wire method and density of the fireworks mixture. An excellent linear relationship has been obtained similar in case of the fireworks raw materials. The correlation is expressed in Eq. (8). Figure 3 shows the temperature dependency of λ_e of the mixture. The λ_e changes a little with temperature.

$$\lambda_e=0.21\rho-0.15 \text{ for the mixture} \quad (8)$$

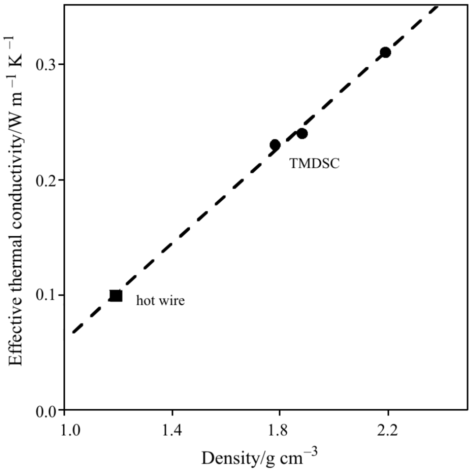

Fig. 2 Relationship between effective thermal conductivity and density for the tested mixture ($KClO_3$/S/$CuSO_4\cdot5H_2O$=7:3:1 mass%) at 313.15 K

At first, we expected that the effective thermal conductivity of the mixture was predictable in the function of λ_e and volume fraction of the ingredients. However, the λ_e of the mixture is quite low like fireworks raw materials and easily measured by the TMDSC method, so no more prediction method is

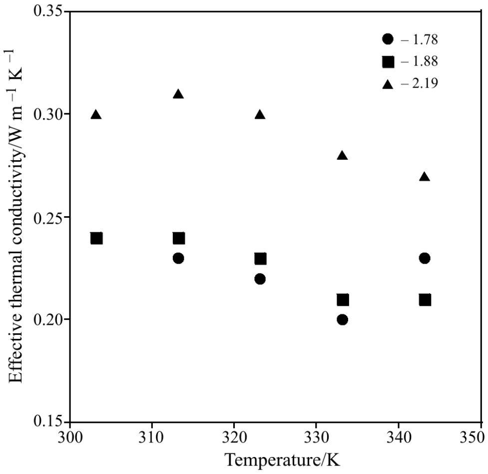

Fig. 3 Effective thermal conductivity as function of temperature for the tested mixture ($KClO_3/S/CuSO_4\cdot 5H_2O$=7:3:1 mass%)

required. Roughly estimating, the λ_e of the mixture, whose particle size is similar to the materials tested in this study, should be from 0.2 to 0.4 W m^{-1} K^{-1}, regardless of the composition.

The mixture used by this research is highly sensitive and easily explodes. So the hot wire method is danger, because it requires a large amount of materials through which an electric current passes. On the other hand, the TMDSC method needs the amount of the sample of about 200 mg, so it is safe for explosive substances.

Conclusions

In this study, effective thermal conductivity (λ_e) of fireworks raw materials and their mixtures have been measured by the TMDSC and the hot wire method, in order to predict spontaneous ignition properties more precisely. As a result, an excellent linear correlation has been obtained between the density and the λ_e by the TMDSC method. The low-density data by the hot wire method lie on the extrapolated point of the linear correlation by the TMDSC method. Accordingly, the λ_e within the ordinary limit of fireworks composition can be measured by the TMDSC method. Three estimation methods of λ_e have been compared. Krupiczka's method shows a good agreement with the experimental values. The TMDSC method needs the amount of the sample of about 200 mg, so it is safe for explosive substances.

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