研究論文

Effect of pressure on the combustion characteristics of tungsten–potassium perchlorate–barium chromate delay powder

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Some combustion experiments and analysis of the combustion residue were carried out to clarify the pressure effect on the burning characteristics of a tungsten – potassium perchlorate – barium chromate delay powder. The results obtained are as follows.

The linear burning rate of the $W/KClO_4/BaCrO_4$ delay composition increased with increasing external pressure, and a fuel-rich composition had a larger burning rate. Additives changed the combustion characteristics and had a different effect according to the composition. The heat of reaction and the maximum combustion temperature increased with increasing external pressure, because of the increase in tungsten oxidation. From the time - temperature history analysis, the addition of diatomaceous earth caused an improvement in heat conduction of the delay powder.

1. Introduction

So-called gas-less pyrotechnic mixtures of tungsten – potassium perchlorate – barium chromate ($W / KClO_4 / BaCrO_4$) have been used in various pyrotechnic devices because of their precise delay time. There have been many studies on these delay compositions, which dealt with combustion characteristics[1] and burning rate modifiers[2]. However, there have been few studies which deal with the pressure effect on the combustion of delay powders.

Delay powders in pyrotechnic devices are used in sealed assemblies. Therefore, a requirement exists for a minimum change in burning rate at the various external pressures. In this study, some combustion experiments, such as burning rate, combustion temperature and heat of reaction, and analysis of the combustion residue were carried out to clarify the effect of pressure on the tungsten – potassium perchlorate – barium chromate delay powder combustion.

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2. Experimental

2. 1 Materials

The sample tungsten powder obtained from a commercial supplier had an average particle diameter of 1.36 μ m. Potassium perchlorate was prepared by pulverizing and sieving a reagent grade material, and its average particle size was about 10 μ m. Barium chromate was a reagent grade with an average diameter of about 1 μ m. Diatomaceous earth and sodium fluoride were reagent grade with an average diameter below 147 μ m.

The delay powders were prepared using an ordinary ball-mill mixer after weighing the ingredients. The formulations of the delay composition are shown in Table 1.

2. 2 Analysis

Qualitative analysis of the reaction residue was performed using common X-ray powder diffraction.

2. 3 Combustion experiments

The delay compositions were burned in an aluminum cylindrical tube, and the time for 10 mm burning was recorded using a digital memory with optical fiber signals. One delay composition divided into nine equal parts was loaded nine times in one delay

Table 1 Formulation of $W/KClO_4/BaCrO_4$ delay composition

Composition (part)			Additive
W	$KClO_4$	$BaCrO_4$	x (part)
64	36	30	0
			D.E. 1
			D.E. 5
			NaF 1
			NaF 5
86	14	30	0
			D.E. 1
			D.E. 5
			NaF 1
			NaF 5
40	60	30	0
			D.E. 1
			D.E. 5
			NaF 1
			NaF 5

x; x part of additive was added to 100 parts of the mixture of W, $KClO_4$ and $BaCrO_4$

D.E.; Diatomaceous earth

tube, and the bulk density was 60% of the theoretical maximum density. The delay tube has an inside diameter of 6 mm, an outside diameter of 15 mm and a 30 mm length. The burning rate was measured in nitrogen atmosphere in the same way as for the heat of reaction and combustion temperature.

A "Shimadzu auto calculating bomb calorimeter" was used to measure the heat of combustion. The sample was loaded in the delay tube and then placed in the bomb before firing. Measurement was carried out in atmospheric and pressurized nitrogen. The combustion temperature was measured with a Pt-Pt/-Rh thermocouple ($\phi = 0.1$ mm) using a Digital Scope DL708 from Hokushin Denki Co., Ltd.

3. Results and discussion

3. 1 Effect of pressure on the combustion of the W / $KClO_4$ / $BaCrO_4$ delay composition

The main reaction of the W / $KClO_4$ / $BaCrO_4$ delay composition is the oxidation of tungsten by potassium perchlorate according to the following

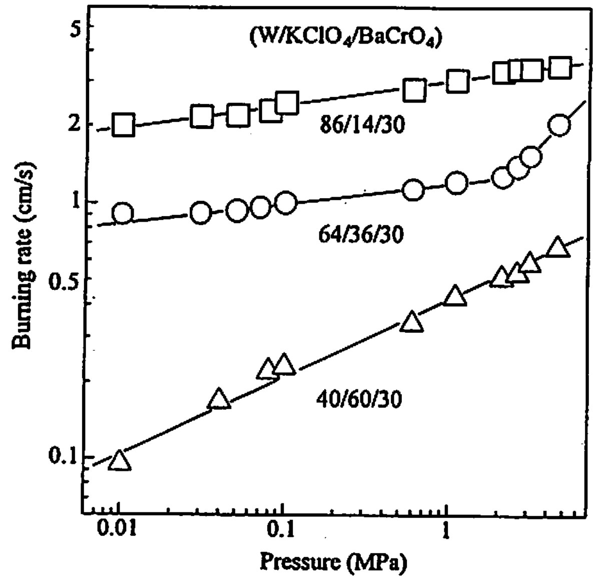

Fig. 1 Effect of pressure on the linear burning rate of the $W/KClO_4/BaCrO_4$ delay composition

equation;

$$4W + 3KClO_4 \rightarrow 4WO_3 + 3KCl \qquad (1)$$

In this study, the delay compositions are classified into three types. One is a tungsten- excess or fuel-rich composition(W / $KClO_4$ = 86/14 by wt.), and the others are a stoichiometric (64/36) and a potassium perchlorate-rich (40/60) composition. Thirty parts of barium chromate were added to 100 parts of the mixture of tungsten and potassium perchlorate by weight. Barium chlomate acts as a burning rate modifier[3].

Fig.1 shows the results of the linear burning rate of the $W/KClO_4/BaCrO_4$ delay compositions in the pressure range of 0.01 MPa ~ 5 MPa. For the delay compositions, the linear burning rate increased with increasing external pressure and increased with increasing tungsten content; the tungsten-excess composition had a few to about twenty times larger value under every external pressure compared to the other compositions. For gasless delays propagation, the thermal conductivity (or thermal diffusivity) of the mixture plays a very important role[4]. Hill and coworker reported that the linear burning rate of solid phase combustion S_L is represented by the following equation using the thermal conductivity λ, heat of reaction q, specific heat C_p, density ρ, reaction zone width w, combustion temperature T_i, ambient temperature Ta and thermal

Table 2 Pressure index of $W/KClO_4/BaCrO_4$ delay composition

Additive (part)		Composition; $W/KClO_4/BaCrO_4$ (part) 64/36/30, Pressure (MPa) 0.01-2.1	64/36/30, 2.1-4.6	86/14/30, 0.01-4.6	40/60/30, 0.01-4.6
	0	0.081	0.613	0.099	0.277
D.E.	1	0.088	0.374	0.092	0.160
D.E.	5	0.081		0.100	0.194
NaF	1	0.093	0.874	0.097	-
NaF	5	0.106	1.061	0.098	0.336

diffusivity α [5),6)].

$$S_L = \lambda q / \{wC_p^2 \rho (Ti-Ta)\} = \alpha [q/\{(wC_p(Ti-Ta)\}] \quad (2)$$

According to this, a fuel-rich composition has a high burning rate because of its large thermal conductivity.

In propellant combustion, the linear burning rate under pressurized conditions S_L is represented by the following Vieille's equation;

$$S_L = bP^n \quad (3)$$

where P is the pressure, n is the pressure index and b is a constant. A linear relation existed between S_L and P in a log-log graph for fuel-rich and potassium perchlorate-rich compositions, but a stoichiometric composition had a break point. The n index values obtained from the decline in Fig.1 are listed in Table 2. A small n index was obtained for a fuel-rich composition below about 5 MPa and for a stoichiometric composition below 2 MPa.

Fig.2 shows the results of X-ray powder diffraction for the combustion residue of a stoichiometric composition. The combustion residue contained unreacted tungsten, barium tungstate($BaWO_4$), potassium chloride and potassium tungsten oxide chloride($K(WO_3)Cl$). The diffraction peak intensity of tungsten became small with increasing external pressure. This indicated a greater extent of tungsten oxidation under high pressure.

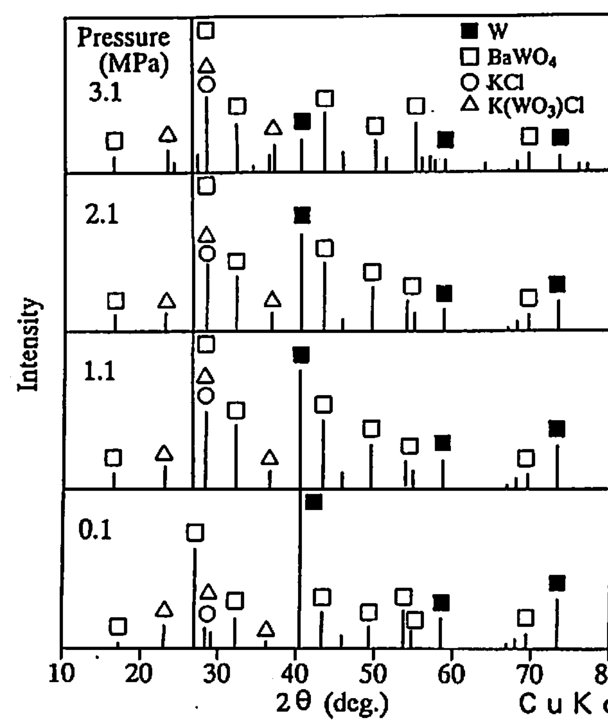

Fig. 2 X-ray powder diffraction of the combustion residue of $W/KClO_4/BaCrO_4$ delay composition.
Full scale of intensity for pressure 3.1 MPa, 2.1, and 1.1; 2000 cps, 0.1; 4000 cps

3.2 Effect of pressure on the combustion of the $W/KClO_4/BaCrO_4$ delay composition with additives

Fig.3 shows the effect of the addition of diatomaceous earth on the burning characteristics of the $W/KClO_4/BaCrO_4$ delay composition under nitrogen atmosphere. The linear burning rate of the $W/KClO_4/BaCrO_4$ delay composition with diatomaceous earth also increased with increasing ambient pressure. However, the addition of diatomaceous earth to a fuel-rich composition decreased the burning rate. On the other hand, the linear burning rate

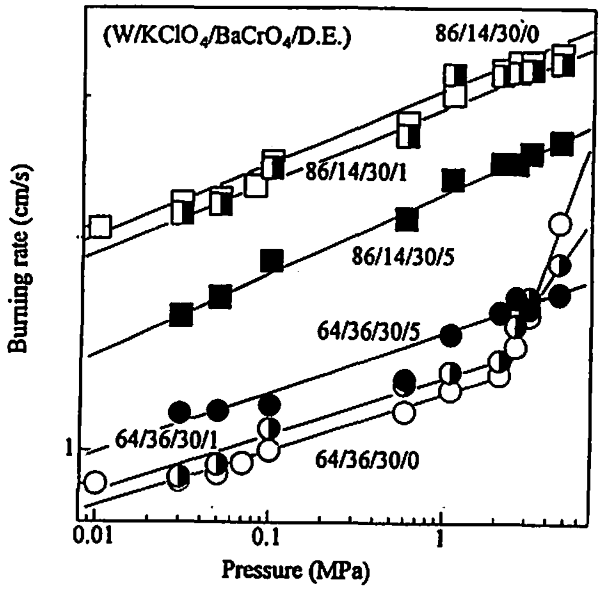

Fig. 3 Effect of addition of diatomaceous earth(D.E.) on the burning characteristics of the $W/KClO_4/BaCrO_4$ delay composition under pressurized nitrogen

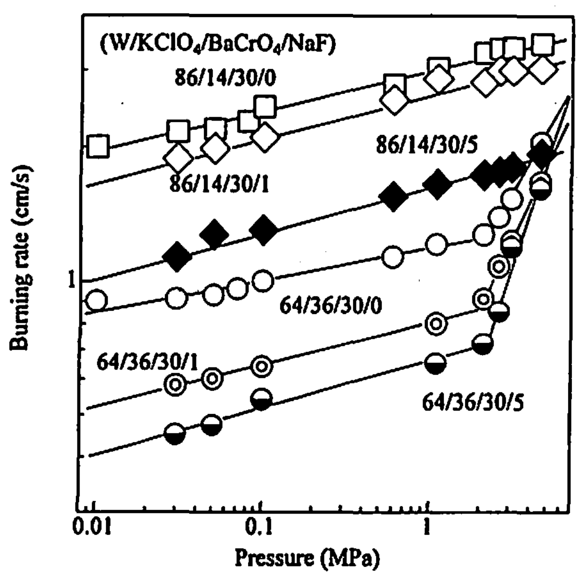

Fig. 4 Effect of addition of sodium fluoride on the burning characteristics of the $W/KClO_4/BaCrO_4$ delay composition under pressurized nitrogen

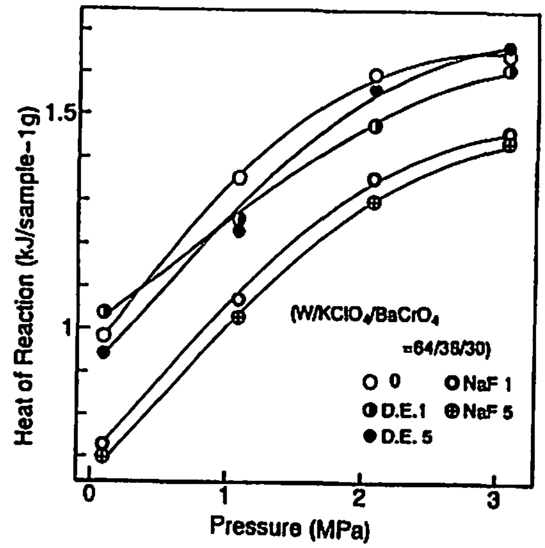

Fig. 5 Effect of pressure on the heat of reaction of the $W/KClO_4/BaCrO_4$/D.E. (Diatomaceous earth) or NaF delay combustion

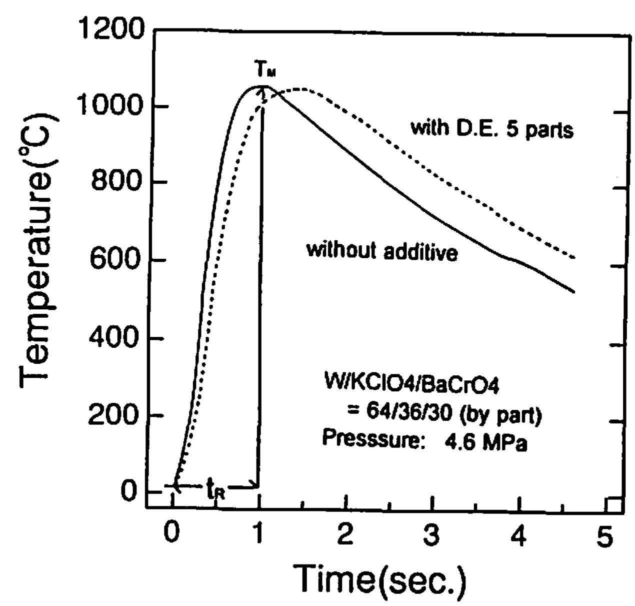

Fig. 6 Example of time - temperature histry for the $W/KClO_4/BaCrO_4$/D.E. delay combustion
T_M: Maximum combustion temperature
t_R: Period which is needed for the temperature to rise up to its maximum at the point where the thermocouple is inserted

of a stoichiometric composition increased with the increasing addition of diatomaceous earth. Moreover, the delay composition of $W/KClO_4/BaCrO_4$/diatomaceous earth = 64/36/30/5 showed a linear relation on Vieille's plots over all pressures differently from that without the additive. Fig.4 shows the effect of the addition of sodium fluoride. On adding sodium fluoride, the linear burning rate decreased for all compositions. The pressure indices of the compositions with and without additives are summarized in Table 2. The pressure index was small for almost all compositions except for a stoichiometric composition under high ambient pressure.

Table 3 Combustion temperature and temperature rise time of the delay composition of $W/KClO_4/BaCrO_4$ = 86/14/30 (by part)

Composition (part) $W/KClO_4/BaCrO_4$/D.E.	Pressure (MPa)	T_M (℃)	t_R (sec)
86/14/30/0	0.1	763	1.35
	1.1	1076	1.40
	2.1	1094	1.55
	2.6	1191	1.50
	3.1	1135	1.40
	4.6	1105	1.40
86/14/30/1	0.1	1027	1.50
	1.1	1051	1.65
	2.1	1054	1.35
	2.6	1084	1.35
	3.1	1081	1.60
	4.6	1075	1.60
86/14/30/5	0.1	818	1.55
	1.1	910	1.40
	2.1	931	1.35
	2.6	977	1.55
	3.1	1025	1.55
	4.6	932	1.65

Table 4 Combustion temperature and temperature rise time of the delay composition of $W/KClO_4/BaCrO_4$ = 64/36/30 (by part)

Composition (part) $W/KClO_4/BaCrO_4$/D.E.	Pressure (MPa)	T_M (℃)	t_R (sec)
64/36/30/0	0.1	872	1.25
	1.1	1065	1.00
	2.1	1034	1.15
	2.6	1141	1.15
	3.1	1077	1.05
	4.6	1058	0.95
64/36/30/1	0.1	854	1.30
	1.1	924	1.20
	2.1	1005	1.25
	2.6	1037	1.20
	3.1	1026	1.15
	4.6	1032	1.10
64/36/30/5	0.1	718	1.35
	1.1	911	1.30
	2.1	991	1.45
	2.6	968	1.25
	3.1	994	1.35
	4.6	1041	1.50

3.3 Effect of the pressure on heat of reaction and combustion temperature

Fig.5 shows the effect of pressure on the heat of reaction of the $W/KClO_4/BaCrO_4$/additive = 64/36/30/x(by wt.) delay combustion. The heat of reaction increased with increasing external pressure. From X-ray powder diffraction of reaction residue, it was confirmed that the extent of oxidation of tungsten became greater under pressurized nitrogen. This caused a high heat of combustion under high external pressure. Additives decreased the heat of reaction.

In a combustion wave, the unreacted layer was heated by thermal conductance. Fig.6 showed the time – temperature history at the point where the thermocouple was inserted for the combustion of the mixture of $W/KClO_4/BaCrO_4$ = 64/36/30 with and without an additive under 4.6 MPa. The time needed for the temperature to rise to maximum temperature (T_M) was designated as t_R (abbreviated as temperature rise time), where the time zero was determined as a time at which the temperature rise of thermocouple commenced. Table 3 and 4 showed the maximum temperature and temperature rise time measured for the composition of $W/KClO_4/BaCrO_4$ = 86/14/30 and 64/36/30 with and without diatomaceous earth under nitrogen atmosphere. Though the fuel-rich composition had a larger values of t_R compared to the stoichiometric composition, it could not be found that the additive had a principal effect on combustion (Table 3). However, if diatomaceous earth was added to the composition of $W/KClO_4/BaCrO_4$ = 64/36/30, the temperature rise time (t_R) of the mixture with additive became longer compared with the data without additives under the same pressure. t_R is dependent on thermal diffusivity and combustion temperature. Therefore, this result means that a large t_R corresponds to a large thermal diffusivity, even though the maximum temperature of the mixture with additive was lower compared with that without additive. From these results, we can conclude that the addition of diatomaceous earth causes an improvement in the thermal diffusivity.

4. Conclusions

The linear burning rate of a $W/KClO_4/BaCrO_4$ delay composition increased with increasing ambient pressure, and a fuel-rich composition had a large burning rate. Addition of diatomaceous earth to a fuel-rich composition decreased the burning rate. On the other hand, the linear burning rate of a stoichiometric composition increased with increasing diatomaceous earth.

The heat of reaction and the maximum temperature increased with increasing external pressure. This was ascribed to the high extent of tungsten oxidation in the composition. From the time - temperature history, the addition of diatomaceous earth caused an improvement in the thermal conductance for a stoichiometric composition.

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タングステン－過塩素酸カリウム－クロム酸バリウム系延時薬の燃焼に及ぼす圧力の影響

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タングステン－過塩素酸カリウム－クロム酸バリウム系延時薬の燃焼に及ぼす圧力の効果を，熱分析，燃焼残留物の分析および燃焼速度や温度などの燃焼特性値を測定することにより検討した。得られた結論は以下の通りである。

タングステン－過塩素酸カリウム－クロム酸バリウム系延時薬の燃焼速度は，圧力とともに上昇した。その際，タングステンを過剰に含む系は大きい燃焼速度を示した。添加物は，燃焼特性を変化させ，この効果は組成により異った。高圧になるほどタングステンの酸化率が上昇し，燃焼熱および燃焼温度も上昇した。温度上昇曲線の解析より，珪藻土の添加は熱伝導性を良くすることが判った。

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