The combustion mechanism of tungsten-potassium perchlorate-barium chromate delay powder

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Thermal analysis, analysis of the combustion residue and combustion characteristics measurement such as burning rate or temperature were carried out to clarify the combustion mechanism of a tungsten - potassium perchlorate - barium chromate delay powder. The results obtained are as follows.

The main reaction of the delay powder of tungsten - potassium perchlorate - barium chromate is the oxidation of tungsten by potassium perchlorate. Barium chromate acts as a burning rate modifier, and the smaller the content the larger is the burning rate.

Three types of delay compositions used in this study show characteristic burning behavior. A stoichiometric or a oxidizer-rich composition has a small linear burning rate, although it has a large heat of combustion. On the other hand, a tungsten-excess or a fuel-rich composition with a small heat of combustion has a larger linear burning rate than the former, showing a small fractional oxidation of tungsten (below 10%) contained in the delay powder. From these results, a surface combustion mechanism is proposed for the combustion mechanism of this delay powder.

1. Introduction

There have been numerous studies which dealt with delay powder combustion from theoretical and practical aspects. With regard to the combustion theory for gasless pyrotechnic mixtures, there are excellent studies by Boddington et al. of the University of Leeds who obtained combustion characteristics such as the burning rate, burning temperature, heat of combustion, thermal diffusivity, and so on from the analysis of temperature profiles[1)~3)].

Ordinarily, combustion phenomena are complicated by the participation of physical and chemical processes. In the case of delay powder combustion, more complicated problems arise because chemical reactions involved are greatly affected by the surface properties of the ingredients such as surface area, crystallinity, the degree of surface oxidation and so on. Thus, it is very difficult to take into account these properties in such theoretical consideration, and carrying out a case study is inevitable to understand the combustion behavior of the individual system. From these reasons, engineers involved with delay element fabrication have been obliged to repeat the endeavors by trial and error. Tungsten - potassium perchlorate - barium chromate ($W/KClO_4/BaCrO_4$) systems represent one of the most famous gas-less pyrotechnic mixtures, and there have been many studies on these delay compositions, which dealt with combustion characteristics[4)] and burning rate modifier[5)]. In this study, thermal analysis, analysis of the combustion residue, burning rate and temperature distribution measurement, and visual observation of the combustion wave were carried out to clarify the combustion mechanism of the tungsten - potassium perchlorate - barium chromate delay powder.

Received on September 3, 1999

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2. Experimental

2.1 Materials

The sample tungsten powder obtained from a commercial supplier had average particle diameters of

1.36, 2.35, 3.63, 5.00 and 9.20 μm. Potassium perchlorate was prepared by pulverizing and sieving a reagent grade material, and its average particle size was about 10 μm. Barium chromate was a reagent grade with an average diameter of about 1 μm.

The delay powders were prepared using an ordinary ball-mill mixer after weighing the ingredients.

2.2 Analysis

Thermal analysis was performed using a RIGAKU DTA-TG simultaneous analyzer, in which the sample weight was 5mg and the heating rate was 20℃/min. under an argon gas stream.

Qualitative analysis of the reaction products were performed using common X-ray powder diffraction.

2.3 Combustion experiments

The delay compositions were burnt in an aluminum cylindrical tube, and the time for 10mm burning was recorded using a digital memory with optical fiber signals. The mixtures were loaded nine times, and the bulk density was 50～80% of the theoretical maximum density. Preliminary experiments show that the linear burning rate decreases with loading density, but that the mass burning rate is constant within a loading of 60～80% of the theoretical maximum density. With regard to the diameter of the delay tube, the linear burning rate is constant above an inside diameter of 5mm.

A "Shimadzu auto calculating bomb calorimeter" was used to measure the heat of combustion for a 1g sample in an argon gas atmosphere, and the combustion products were analyzed by the method described above.

2.4 Temperature, pressure and thermal constants measurement

The combustion temperature was measured by a high speed video system TVS-4000 from Nippon Avionics Co., Ltd.

Visual observation of the combustion wave was carried out using a "Nac High Speed Video Camera HSV-200."

Thermal diffusivity and specific heat measurements were carried out with a "Laser-Flash Thermal Constant Analyzer TC 3000" from SINKU-RIKO Inc.

The proceeding gas pressure before the flame wave was measured using an "Electromagnetic Oscillograph " and a "High Capacity Pressure Transducer PGM-2KC" from KYOWA DENGYO, Inc. inserted into a confined void space at the opposite end of the combustion wave.

3. Results and discussion

3.1 Effect of some factors on the burning rate of the $W/KClO_4/BaCrO_4$ delay composition

The burning characteristics of the delay composition is affected by (1) thermal conductance, (2) chemical reaction rate, (3) heat loss, (4) movement of gases and (5) ambient temperature and pressure etc. Thermal conductance depends on the type of delay composition and method of loading.

Fig. 1 shows the dimension-less burning rates described on triangle diagrams, in which the burning rate of 40/30/30 having a value of 0.562cm/s is set equal to 1.00 as a standard dimension-less rate. $W/KClO_4/BaCrO_4$ delay compositions have a wide range of burning rate according to the composition. For example, a tungsten-rich composition $W/KClO_4/BaCrO_4$ = 82/9/9 (by weight) has a burning rate of 3.02cm/sec. On the other hand, the burning rate of the composition 24/35/41 is 0.112cm/s. These results also show that the greater the tungsten content the larger is the linear burning rate compared with a constant barium chromate content. Fig. 2 shows a relationship between the burning rate and the tungsten

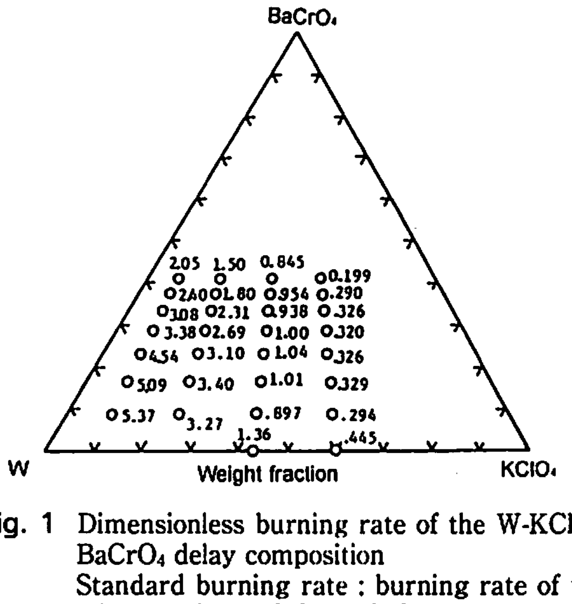

Fig. 1 Dimensionless burning rate of the $W\text{-}KClO_4\text{-}BaCrO_4$ delay composition
Standard burning rate : burning rate of the mixture of $W/KClO_4/BaCrO_4$ = 57/43/40 (by weight) = 1.00, material and inside diameter of delay tube ; 6mm ϕ of aluminum tube, loading density : 60% of theoretical maximum density

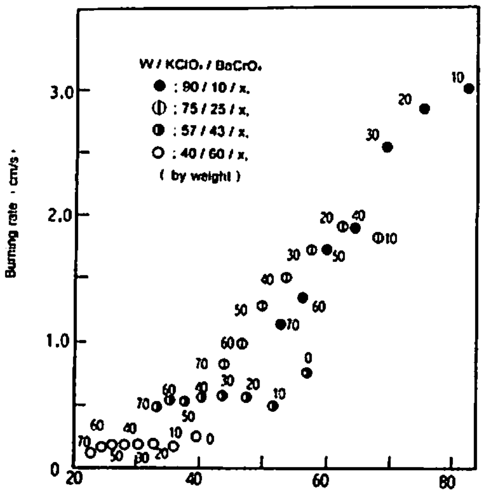

Fig. 2 Relationship between the burning rate and the tungsten content for a $W/KClO_4/BaCrO_4$ delay composition

content for a $W/KClO_4/BaCrO_4$ delay composition. The good linearity indicates that the burning rate depends on tungsten content. Metal tungsten has high thermal conductivity compared to potassium perchlorate or barium chromate, and tungsten-rich composition also has high thermal conductivity. The relation between thermal conductivity and the burning characteristics will be stated in 3.2.

The chemical reaction rate depends on the delay composition, the particle size (especially, the size of the reducing agent) and method of loading. Fig. 3 shows the effect of particle size on the linear burning rate for $W/KClO_4/BaCrO_4$ (90/10/x, 75/25/x and 57/43/x (x=10 by weight) delay composition. These results show that the larger the particle size of tungsten the lower is the linear burning rate for every composition.

The heat loss which arises due to conduction and radiation to the atmosphere is affected by the diameter of the delay tube, the material of tube, method of loading and combustion temperature. As stated before, preliminary experiments show that the linear burning rate is constant above an inside diameter of 5mm. So, it is concluded that above 5mm the heat loss effect is negligibly small to affect the combustion characteristics.

Movement of gases in the loaded delay tube depends on the method of loading. Fig. 4 shows the effect of loading on the preceding gas pressure before the flame. There is no preceding gas over 80% of the theoretical density. Moreover, the mass burning rate is constant at a loading of 60～80% of the theoretical maximum density. From these results, it can be concluded that there is no preceding gas at above 80% loading relative to the theoretical maximum density and a small effect on combustion at 60～80% loading.

The linear burning rate of $W/KClO_4/BaCrO_4$

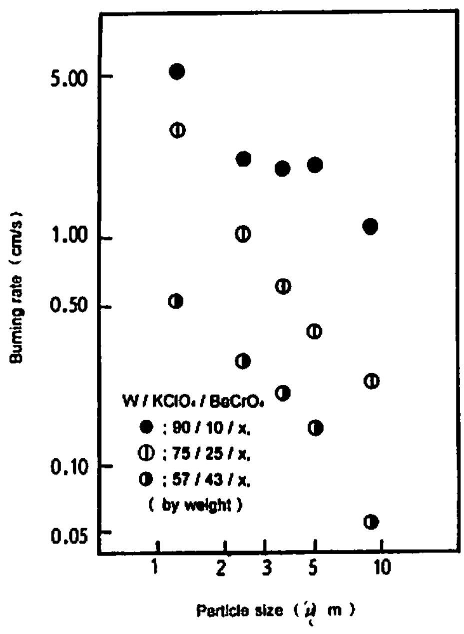

Fig. 3 Effect of particle size on the linear burning rate of the $W/KClO_4/BaCrO_4$ delay composition

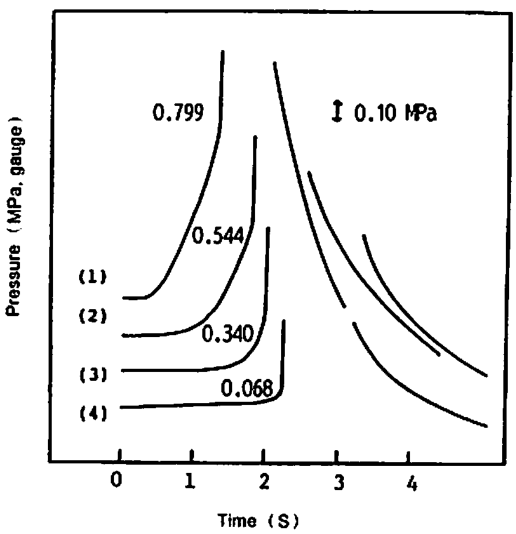

Fig. 4 Effect of loading on the pressure rise in the space before the combustion wave of the W-$KClO_4$-$BaCrO_4$ delay Composition ; $W/KClO_4/BaCrO_4$ = 30/25/45 (by weight), loading density ; (1) 50%, (2) 60%, (3) 70% and (4) 80% of theoretical maximum density

increased with an increasing ambient temperature and pressure, but these effects were not considered in the present work.

3.2 Combustion mechanism of the W/$KClO_4$/$BaCrO_4$ delay composition

Fig. 5 shows the burning rates, temperatures and schematic representations of the front of combustion waves which were obtained by delay combustion of a normal loading, a bored loading with a diameter of 1mm and inserted loadings of metal wires. Every type of loading causes a very different linear burning rate, though resulting in the same combustion temperature. A bored loading with a diameter of 1mm has a larger linear burning rate than a normal loading. For inserted loadings of metal wire, the burning rate is increased with the increasing thermal conductivity of the wire. These resaults also show a important role of thermal conductance on the burning rate of delay powder.

The temperature profiles are shown in Fig. 6, in which the structure of the combustion wave and related chemical reactions deduced from thermal analysis, analysis of the reaction residues and visual observation are also described. The combustion wave consists of (1) a luminescence zone where the main reaction occurs, (2) a melting zone with a green color where the subsequent reaction of the reaction product with barium chromate and (3) a bulk reaction zone with a red-hot heat where the maximum combustion is attained.

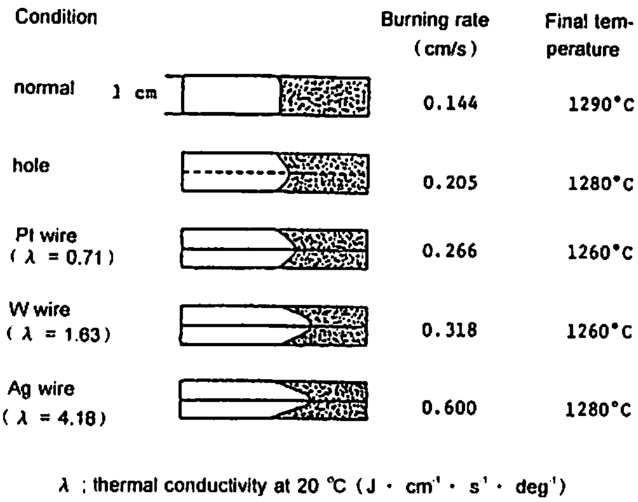

Fig. 5 Schematic representation of the burning wave front for the W-$KClO_4$-$BaCrO_4$ delay combustion

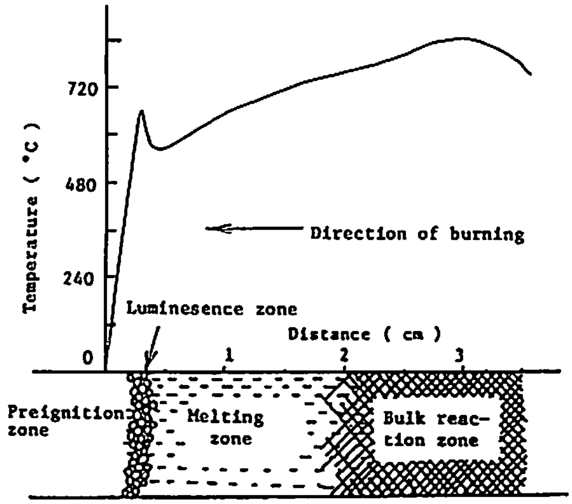

Fig. 6 The structure of the combustion wave of the W-$KClO_4$-$BaCrO_4$ delay combustion

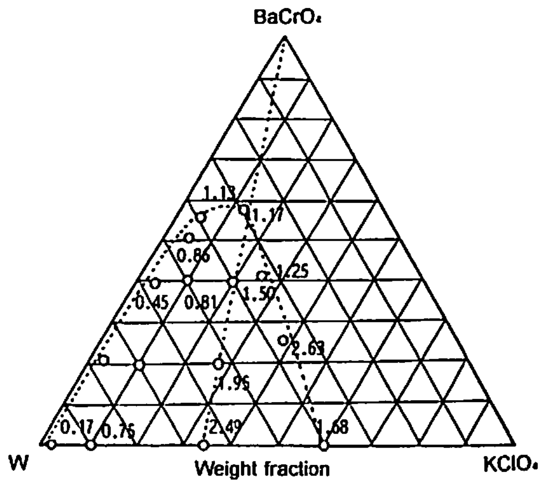

Fig. 7 Heat of combustion of the W-$KClO_4$-$BaCrO_4$ delay composition (kJ/mol)

Fig. 7 shows the heat of combustion for the compositions of fuel-rich, oxidizer-rich and stoichiometric compositions for the reaction of tungsten and potassium perchlorate of a W/$KClO_4$/$BaCrO_4$ delay composition. The solid line in the center of the diagram corresponds to the stoichiometric condition of tungsten and potassium perchlorate which causes the main reaction of this delay compositions. Comparing the heat of combustion, delay powders which have a stoichiometric composition show a large heat of combustion, and tungsten-rich conditions have a very small value, although these have a large linear burning rate.

As stated before, the burning rate depends on tungsten content showing the good linearity between thermal conductivity and the burning rate. This is interpreted from the point of the thermal diffusivity or the thermal conductivity of the delay powder because these thermal constants highly depend on the amount of tungsten. From the theory of Mallad and Le-Chatelier, the following equation can express the linear burning rate for the laminar flame of a gas phase combustion S_L using thermal conductivity λ, specific heat C_p, density ρ or thermal difusivity α [6].

$$S_L \sim (\lambda / C_p \rho)^m (\text{Reaction rate})^n = (\alpha)^m (\text{Reaction rate})^n$$

Circumstances for a solid state combustion are very different from those for a gas phase combustion. The applicability of this equation was examined, assuming that this delay composition causes an ideal combustion like a gas phase combustion. Fig.8 shows a relationship between the burning rate and thermal diffusivity for a $W/KClO_4/BaCrO_4$ delay composition. The good linearity indicates an important effect of thermal diffusivity on combustion.

4. Discussion

The $W/KClO_4/BaCrO_4$ delay composition caused the oxidation of tungsten by potassium perchlorate in front of the combustion wave. This tells us that the main reaction for the delay powder of $W/KClO_4/BaCrO_4$ is

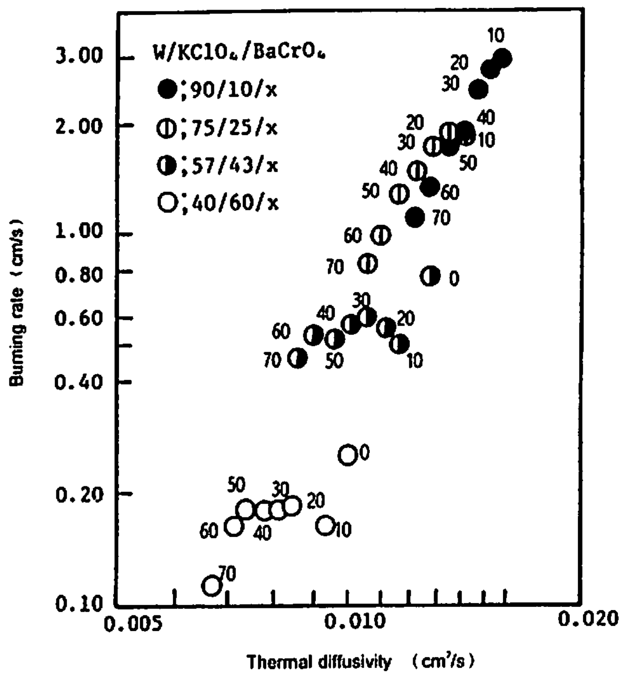

Fig. 8 Relationship between burning rate and thermal diffusivity of the $W\text{-}KClO_4\text{-}BaCrO_4$ delay combustion

Table 1 The structure of combustion wave and related reactions for $W/KClO_4/BaCrO_4$ delay compositions

Luminesence zone with white light
$4W + 3KClO_4 \rightarrow 4WO_3 + 3KCl$
Melting zone with green color
$WO_3 + KCl \rightarrow K\ (WO_3)\ Cl$ or $K_{0.57}WO_3$
$4WO_3 + 4BaCrO_4 \rightarrow 4BaWO_3 + 2Cr_2O_3 + O_2$
Bulk reaction zone with red-hot heat
$4W + BaCrO_4 \rightarrow BaWO_4 + 2Cr_2O_3 + BaO$

the oxidation of tungsten by potassium perchlorate. Barium chromate acts as a burning rate modifier, and the smaller the content the larger is the burning rate.

In this study, delay compositions are classified into tree types. One is a tungsten- excess or fuel-rich, and the others are a stoichiometric and a potassium perchlorate-rich composition. The 37/38/25 (by weight) delay composition of $W/KClO_4/BaCrO_4$ has a linear burning rate of 0.25cm/sec and a large heat of combustion of 2630Joule/g. On the other hand, the $W/KClO_4/BaCrO_4$ = 75/4/21 (by weight) tungsten-excess mixture has about a 10 times larger linear burning rate of 2.72cm/sec. However, the heat of combustion of this mixture is a very small value of 405 Joule/g.

Delay compositions which contain metal wire and have a high tungsten content show a large burning rate, and linear relationships exist between the burning rate and thermal diffusivity. These tell us that thermal conductance acts as very important role for this delay combustion. Besides, a high tungsten content composition with a small heat release shows a large burning rate, although the fractional oxidation of tungsten remains small. That is, the oxidation of tungsten does not exceed 10% for the 90/10 $W\text{-}KClO_4$ delay combustion and is restricted only on its surface. From these results, a surface combustion mechanism is proposed for the combustion mechanism of this delay powder. Actually, the delay composition with a high percentage of ingredient whose thermal conductivity or thermal diffusivity is very high shows the large linear burning rate. Manganese or boron containing delay composition is another good example, in which the combustion wave proceeds through surface combustion mechanism showing high linear burning rate.

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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機構

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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機構を明らかにするために，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など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主反応は，過塩素酸カリウムによるタングステンの酸化である。クロム酸バリウムは燃焼調整剤として働き，その量が多ければ燃焼速度は小さくなる。この主反応の等量組成あるいは酸化剤が過剰な組成では燃焼熱は大きいが，燃焼速度は小さい。これに対して，タングステン（燃料）過剰の組成では燃焼熱は小さいが，燃焼速度は前者の数倍にもなった。この場合に燃料タングテンの酸化率は非常に小さく，10％以下である。これらの結果から，この系の燃焼機構として表面燃焼機構が提案された。

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