研究論文

The reactivity of sodium chlorate and iron powder mixtures

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The mixture of sodium chlorate with iron powder has been used as a base material for an oxygen generating agent during emergencies. In this study, a thermal analysis, an analysis of reaction residue and combustion experiments such as combustion calorimetry or burning rate measurements were carried out to clarify the thermal reaction and combustion reaction of the sodium chlorate - iron powder mixture.

The binary mixture, which contained fine iron powder, had a good reactivity at low temperature and the capability of large oxygen release. The binary mixtures consisting of sodium chlorate and fine iron powder were combustible over a wide range of iron content from 20~to 60 wt.% iron. Iron oxide had a large catalytic effect on the thermal reaction of the binary mixture. However, the catalytic effect on combustion depended on the species of iron oxides. Fe_2O_3 with fine particle size had a large catalytic effect. The addition of diatomaceous earth, sodium perborate and strontium peroxide also increased the linear burning rate. Moreover, diatomaceous earth improved the reproducibility of the linear burning rate.

1. Introduction

Chlorate besides perchlorate is one of the high oxygen containing materials and has the characteristic feature of loosing this oxygen relatively easily compared to perchlorate. Based on these reasons, sodium chlorate ($NaClO_3$) has been used as a base material as an emergency oxygen generating agent[1)~3)]. However, because of an insufficient heat of decomposition ($-\Delta H$ = 578 J/g), it is not combustible by itself. Usually, sodium chlorate can perform a sustained combustion, but only when iron powder (Fe) as a heat generating agent, iron oxide as the catalyst (Fe_2O_3) and some additives are added.

A colored smoke composition, which consists of chlorate and an organic compound, is famous as a chlorate containing combustion mixture. However, there have been few studies which dealt with the mixture of chlorate with metal. In this study, a thermal analysis, the analysis of the reaction residue and combustion experiments such as combustion calorimetry or burning rate measurements were carried out to clarify the thermal reaction and combustion reaction of the sodium chlorate - iron powder mixture.

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2. Experimental

2.1 Materials

Three types of iron powder samples obtained from a commercial supplier had average particle diameters of 1.36 μm (fine, Fe(1)), 6.99 μm (Fe(2)) and 62.4 μm (Fe(3)). Sodium chlorate was prepared by pulverizing and sieving a reagent grade material, and its average particle size was about 75 μm.

The iron oxide catalysts obtained from a commercial supplier had average particle diameters of 8.6 μm (Fe_2O_3(1)), 16.8 μm (Fe_2O_3(2)) and 0.5 μm (Fe_3O_4). The diatomaceous earth was reagent grade with an average diameter below 147 μm. Sodium perborate and strontium peroxide were prepared by pulverizing and sieving reagent grade material, and their average particle size were about below 147 μm.

The mixtures were prepared using an ordinary ball-mill mixer after weighing the ingredients. The basic formulations of the mixtures have the compositions of $NaClO_3$/Fe =80/20,70/30,60/40, 48.8/51.2,45.9/54.1 and 38.9/61.1(by weight). The mixtures of $NaClO_3$ / Fe =48.8/51.2, 45.9/54.1 and 38.9/61.1 correspond to the stoichiometric compositions according to Eqs.(1)~ (3), respectively.

$$NaClO_3 + 2\ Fe \rightarrow NaCl + Fe_2O_3 \quad (1)$$

$$NaClO_3 + 9/4\ Fe \rightarrow NaCl + 3/4\ Fe_3O_4 \quad (2)$$

$$NaClO_3 + 3\ Fe \rightarrow NaCl + 3\ FeO \quad (3)$$

The catalyst and additive were added by 1 ~10 parts to 100 parts of the binary mixture by weight.

2.2 Analysis

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

Thermal analysis was performed in argon using a Rigaku DTA-TG Simultaneous Analyzer TAS-200 under atmospheric conditions with a heating rate of 20℃/min. The sample weight was 3 mg, and the sample container was a 5 mm high × 5 mm Φ cell made of alumina.

2.3 Combustion experiment

The mixtures were burned in an aluminum cylindrical tube, and the time for a 10 mm burning was recorded using a digital memory with optical fiber signals. One oxygen generating composition divided into nine equal parts was loaded nine times in one tube, and the bulk density was 60% of the theoretical maximum density. The tube had an inside diameter of 4~8 mm, outside diameter of 15 mm and 30 mm length. The measurement was carried out in atmospheric and pressurized nitrogen similar to the heat of reaction and combustion temperature.

A "Shimadzu auto calculating bomb calorimeter" was used to measure the heat of combustion. The sample weight was about 1.2 g and 0.2 g of a boron-potassium nitrate igniter was used in order to ensure firing. The measurement was carried out in atmospheric and pressurized nitrogen. The combustion temperature was measured by a W/W-Rh5-20% thermocouple (ϕ = 0.25mm) using a Digital Scope DL708 from Hokushin Denki Co., Ltd.

3. Results and discussion

3.1 Thermal reactivity of sodium chlorate, iron powder and their mixture

Fig.1 shows the DTA and TG traces of iron powders in air. The oxidation of iron powder in air showed quite different features depending on the particle sizes. Fine particle iron powder Fe(1) was oxidized at temperatures ranging from 235 to 500℃ with a weight increase of about 30 %. On the other hand, iron powder Fe(3) with particle size of 62.4μm was oxidized at temperatures ranging from 380 to 800℃ with a weight increase of about 42 %(Fe(2); 44 %). Complete oxidation to Fe_2O_3, Fe_3O_4 and FeO correspond to 43.2, 38.2 and 28.7% weight increases, respectively. The X-ray diffraction patterns of the reaction residue after oxidation of Fe(1) contained iron (Ⅱ) oxide (FeO) and iron (Ⅱ) iron (Ⅲ) oxide(Fe_3O_4). Therefore, fine iron powder Fe(1) suffered from insufficient oxidation. Based on these results, it was concluded that iron powder with a fine particle size was easy to oxidize, but the extent of oxidation was small compared to the larger particles.

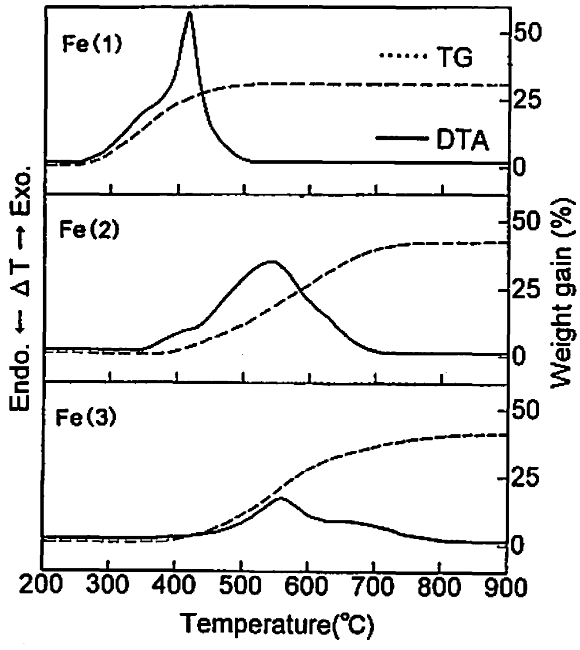

Fig. 1 DTA and TG curves of iron powders in air

Fig.2 shows the DTA and TG traces of sodium chlorate and its mixtures with iron powders in argon. The DTA trace of sodium chlorate showed an endothermic peak at 255℃caused by melting and a wide exothermic decomposition peak ranging from 365 to 615℃with a weight decrease. This decomposition involved the following stepwise reactions[4].

$$4\,NaClO_3 \rightarrow 3NaClO_4 + NaCl \quad (4)$$

$$NaClO_4 \rightarrow NaCl + 2O_2 \quad (5)$$

The reaction of the binary mixture also occurred stepwise and the temperature at which the reaction commenced became lower with a decrease in the particle size of the iron powder. The weight decrease of the binary mixtures of $NaClO_3$/Fe(1), $NaClO_3$/Fe(2) and $NaClO_3$/Fe(3) were 19 wt.%, 11% and 10%, respectively. The extent of oxidation determined by the X-ray diffraction for the reaction residue after the reaction was 14%, 50% and 55% for $NaClO_3$/Fe(1), $NaClO_3$/Fe(2) and $NaClO_3$/Fe(3), respectively.

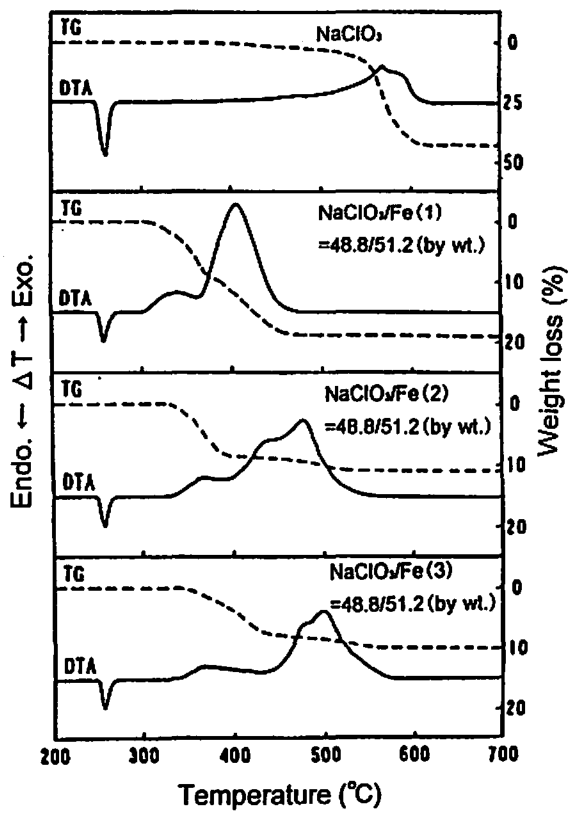

Fig. 2 DTA and TG curves of $NaClO_3$ and its mixtures with iron powders in argon

Therefore, the binary mixture which contained iron powder having a fine particle size had a good reactivity at low temperature and the capability of a larger oxygen release.

3.2 Combustion of the mixtures containing sodium chlorate and iron powders

The heat of combustion and combustion temperature are important characteristics when designing a combustion system. Fig.3 shows the heat of combustion of the binary mixtures of sodium chlorate with iron powders. The heat of combustion of the binary mixtures had a maximum value at the iron content below 51.2 wt.% which corresponded to the stoichiometric composition of Eq.(1). From the X-ray powder diffraction, the combustion residue contained iron (II) oxide (FeO) for the iron-rich composition, and iron(II) oxide (FeO) and iron(II) iron(III) oxide (Fe_3O_4) for the sodium chlorate-rich composition. Therefore, it was found that the maximum oxidation state of iron (iron(III) oxide, Fe_2O_3)) was not attained in this combustion system. Fig.4 shows the combustion temperature of the binary mixtures of sodium chlorate with iron powders The combustion temperature of the binary mixtures had a maximum value of 1420℃ at the same composition as that of the maximum heat of reaction.

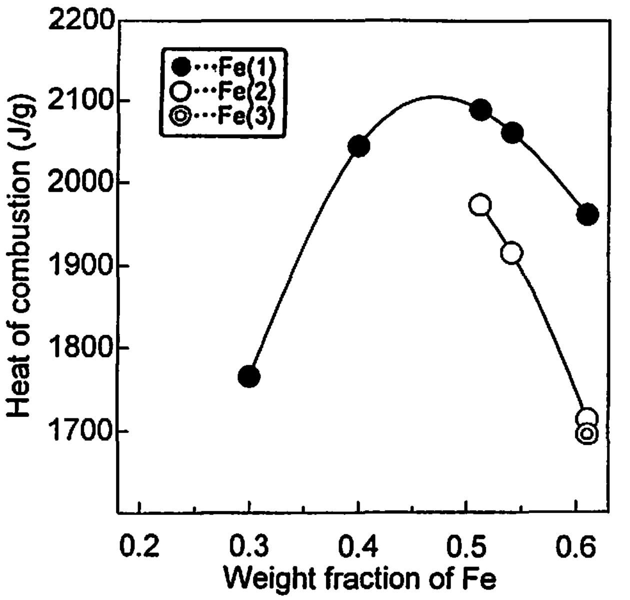

Fig. 3 Heat of combustion of the binary mixtures of $NaClO_3$ with iron powders

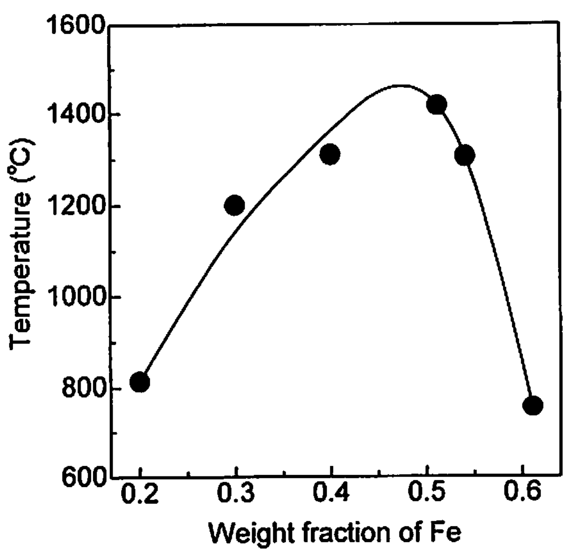

Fig. 4 Combustion temperature of the binary mixtures of $NaClO_3$ with iron powders

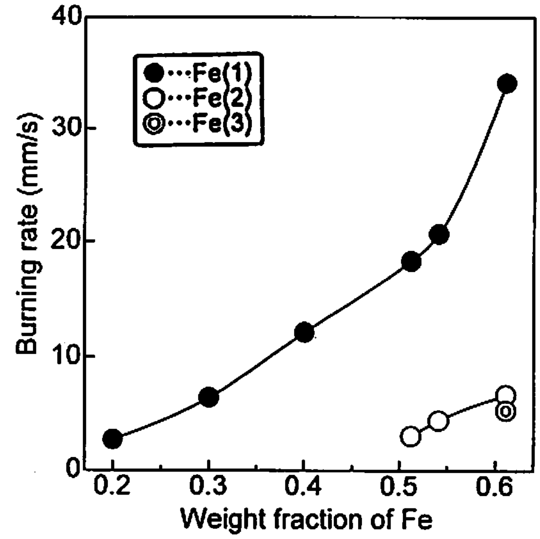

Fig. 5 Linear burning rate of the mixtures of $NaClO_3$ with iron powders

Fig.5 shows the linear burning rate of the mixtures of sodium chlorate with iron powders of various particle sizes. The binary mixtures consisting of sodium chlorate and fine iron powder were combustible over a wide range of iron content which contained 20~60 wt.% of iron, and the linear burning rate increased with an increase in the iron content. On the other hand, iron powder with a larger particle size had a small linear burning rate and its flammability limit was narrow. Based on these results, it was found that the activity of iron powder was an important factor to maintain a sustained combustion. Metal fuel plays two important roles to propagate the combustion wave. One is to increase in burning rate with its high exothermicity, and the other is the heat transfer effect from the combustion zone to the unreacted layer because of the high thermal conductivity. In this experiment, it was recognized that the latter had a larger effect on combustion because of the high burning rate of the iron-rich composition.

3. 3 Effect of catalyst addition on the reactivity of the mixtures of sodium chlorate with iron powders

Metal oxides are capable of catalyzing the alkali metal chlorate decomposition[5]. Thermal analysis of the mixture with a 5% iron oxide catalyst (Fe_2O_3(1))showed that the exothermic reaction commenced immediately after the melting of the sodium chlorate and that completed at 400℃. Other catalysts catalyst (Fe_2O_3(2) and Fe_3O_4) also had the same catalytic effect on the thermal reaction of the binary mixture.

As an oxygen gas generating agent, the most desirable composition is the one able to obtain the maximum amount of oxygen evolution. From previous experiments, the mixture of $NaClO_3$/Fe =80/20(by wt.)resulted in the maximum oxygen evolution among the combustible formulations. Therefore, the catalytic effect of iron oxide (Fe_2O_3(1)) on the linear burning rate of the binary mixtures was examined for this composition. Fig.6 shows the results of the combustion experiments in which x parts catalyst was added to 100 parts of the mixture of $NaClO_3$/Fe(1)= 80/20(by wt). The addition of the iron oxide catalyst made the linear burning rate about 2.3(10% addition)~3.3 (5 % addition) times larger compared to that without a catalyst. However, the other catalyst of Fe_2O_3(2) (Fig.7) and Fe_3O_4 had a small effect on burning rate increase.

3. 4 Effect of additive on the burning characteristics of the mixtures of sodium chlorate with iron powder

Fig.8 shows the effect of diatomaceous earth addition on the linear burning rate of the mixtures of sodium chlorate with iron powder in which x parts of diatomaceous earth was added

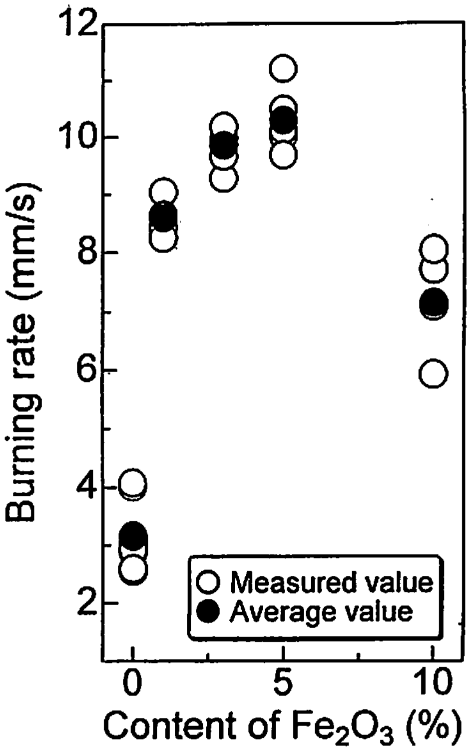

Fig. 6 Effect of addition of iron oxide (Fe_2O_3(1)) on the linear burning rate of the mixtures of $NaClO_3$ and Fe(1)
(x parts of iron oxide (Fe_2O_3(1)) was added to 100 parts of the mixture of $NaClO_3$/Fe(1) = 80/20 by wt.)

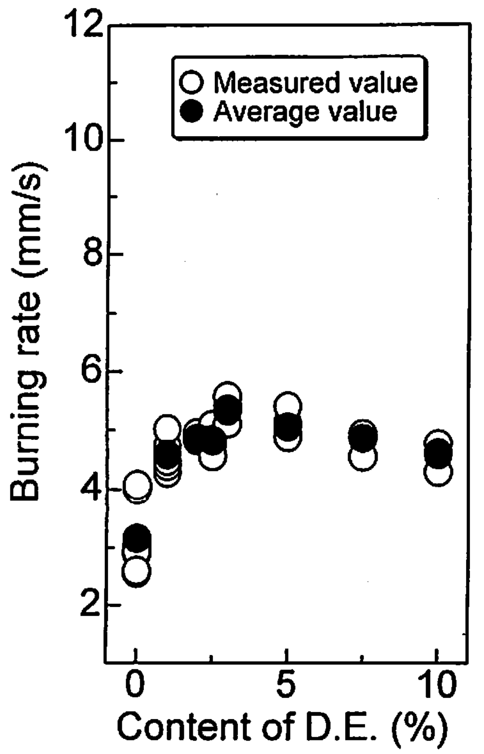

Fig. 8 Effect of addition of diatomaceous earth on the linear burning rate of the mixtures of sodium chlorate with Fe(1)
(x parts of diatomaceous earth was added to 100 parts of the mixture of $NaClO_3$/Fe(1) = 80/20 by wt.)

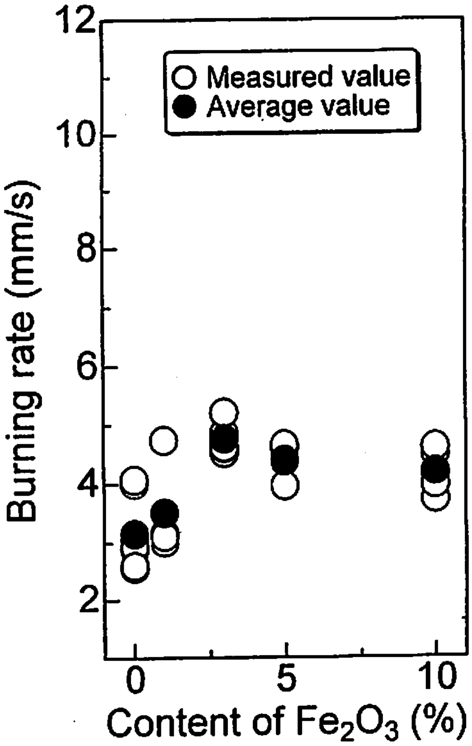

Fig. 7 Effect of addition of iron oxide (Fe_2O_3(2)) on the linear burning rate of the mixtures of $NaClO_3$ and Fe(1)

to 100 parts of the mixture of $NaClO_3$/Fe(1) = 80/20(by wt.). The addition of diatomaceous earth increased the linear burning rate 1.3~1.7 times higher compared to that of the binary mixture. Moreover, the binary mixture and the binary mixture with the iron oxide catalyst did not have a very reproducibility with respect to the linear burning rate. For example, the average value of the linear burning rate was 3.1 ±1.3 mm/sec for the binary mixture, and 11.1 ±1.1 mm/sec for the binary mixture with 5 parts of iron oxide catalyst. On the other hand, the linear burning rate of the binary mixture with diatomaceous earth had a good reproducibility and the average value of the linear burning rate was 5.0 ±0.2 mm/sec for a 5 part addition.

Fig.9 shows the effect of the addition of sodium perborate on the heat of reaction of the mixtures of sodium chlorate with iron powder, in which x parts of strontium peroxide was added to 100 parts of the mixture of $NaClO_3$/Fe(1)= 80/20 (by wt.). The addition of sodium perborate increased the linear burning about 3 times higher

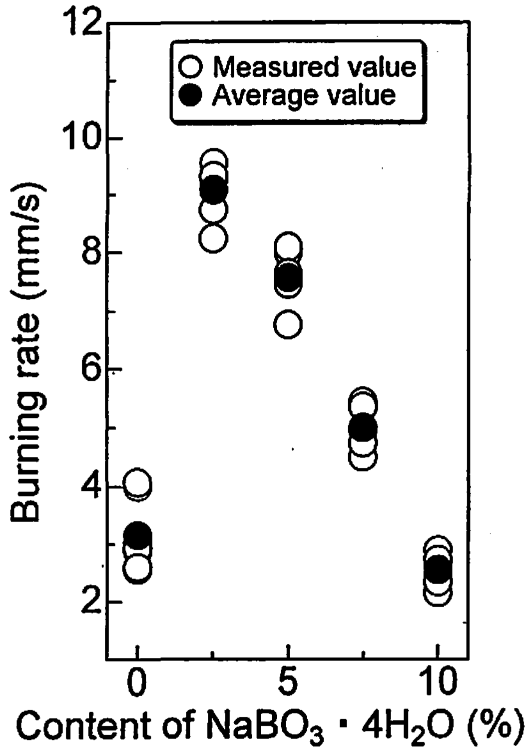

Fig. 9 Effect of addition of sodium perborate on the linear burning rate of the mixtures of sodium chlorate with Fe (1)

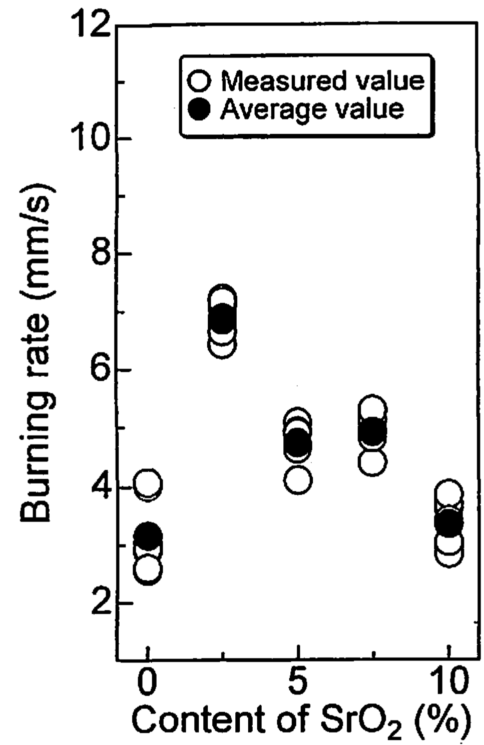

Fig. 10 Effect of addition of strontium peroxide on the linear burning rate of the mixtures of sodium chlorate with Fe (1)

for a small amount 2.5 % of addition compared to that without any addition. Strontium peroxide also increased the linear burning rate about 2.2 times higher with the 2.5 % addition (Fig.10). The decomposition temperatures of sodium perborate and strontium peroxide, at which time the decomposition commences, are 80 and 330℃, respectively[6]. The precise investigation of the role of the additives was not carried out in this experiment. However, the high thermal reactivity of the additives may be ascribed to the improvement of the combustion characteristics of the binary mixture of sodium chlorate with iron powder, even for a small amount of addition.

4. Conclusions

The reaction of the binary mixture of sodium chlorate with iron powder occurred stepwise and the temperature at which the reaction commenced became lower with a decrease in the iron powder particle size. A binary mixture which contained fine iron powder had a good reactivity at low temperature and the capability of a large oxygen release due to its uncompleted oxidation. The binary mixtures consisting of sodium chlorate and fine iron powder were combustible over the wide range of iron content which contained 20～60 wt.% of iron, and the linear burning rate increased with an increase in the iron content.

Certain kinds of the iron oxides catalyzed the thermal decomposition of sodium chlorate. However, the catalytic action of the iron oxide catalyst on the combustion was different with respect to its species and the iron oxide (1) had a large catalytic effect on the combustion. The addition of diatomaceous earth, sodium perborate and strontium peroxide increased the linear burning rate of the binary mixtures of sodium chlorate with the iron powder. Moreover, the diatomaceous earth improved the reproducibility of the linear burning rate.

References

1) K. Kakiuchi, S. NISHII, M. AKIYOSHI, H. NAKAMURA and Y. HARA, "Proceedings of 1998 Spring Symposium on Jananese Explosives Society (1998) p.117

2) S. KUROSE, Y. KANEKO, A. KIDO and M. KUSAKABE, "Proceedings of 1987 Spring Symposium on Jananese Explosives Society (1987) p.113

3) S. KUROSE, Y. KANEKO, A. KIDO and M. KUSAKABE, "Proceedings of 1986 Autamn Symposium on Jananese Explosives Society (1987) p.13
4) F. Solymosi, "Structure and stability of salts of halogen oxy acids in the solid phase", John Wiley & Sons (1977) p.35
5) ibid., P.49
6) T. NAGAISHI, M. TOHBO, J. YOSHINAGA, M. MATSUNOTO and S. YOSHINAGA, Kogyo Kayaku, 42(5), 304(1981)

塩素酸ナトリウム－鉄系組成物の反応

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塩素酸ナトリウム－鉄系組成物は緊急脱出用の酸素ガス発生剤の主剤として用いられている。本研究では，この組成物の熱反応および燃焼反応性を，熱分析法，燃焼残留物の分析および燃焼試験などにより検討した。

微粒子の鉄粉を用いた塩素酸ナトリウム－鉄系組成物は，他の鉄粉を用いた組成物よりも低温で反応し，酸素ガス発生能力も大きかった。この二成分系組成物は，粒子径が1.36 μm の細かい鉄粉を用いた場合，鉄の含有量が20～60wt.%の広い範囲で燃焼可能であった。酸化鉄，珪藻土，過ホウ酸ナトリウムおよび過酸化ストロンチウムの添加は燃焼速度を増大させた。また，珪藻土の添加は燃焼速度の再現性を向上させた。

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