The reactivity of magnesium-oxidizing agent pyrolants

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A "Pyrolant" is a mixture which consist of a metal fuel and an oxidizing agent functioning as both a propellant and a pyrothenic and which undergoes a reaction evolving high energy and a large amount of gas at high temperature. In this report, the thermal reaction and the combustion of the magnesium - containing pyrolants, which are mixtures of magnesium with oxidizing agents, were studied by thermal analysis, analysis of combustion residues, burning rate measurements and visual observation of combustion. The results obtained are as follows :

The thermal reactivity of a magnesium-containing pyrolant varies considerably with the species of oxidizing agent. The magnesium- ammonium nitrate pyrolant was very thermally reactive and the magnesium - potassium nitrate pyrolant caused an exothermic reaction at a higher temperature of about 450℃. However, the linear burning rate of magnesium - potassium nitrate was about 6 times as fast as that of the magnesium - ammonium nitrate or ammonium perchlorate pyrolant. Therefore, no apparent relation was found between the thermal reactivity and the burning rate.

1. Introduction

The magnesium (abbreviated as Mg) - oxidizing agent mixture has been utilized in the field of pyrotechnics and fireworks. Many researchers have reported on the reaction and combustion phenomenon of this composition. However, there are many problems unclarified about the low temperature reaction causing spontaneous ignition, the mechanism of the thermal reaction and the detailed combustion characteristics for these compositions.

Kuwahara et al. gave a definition of the term "pyrolant" as a mixture which consisted of a metal fuel and an oxidizing agent functioning as both a propellant and a pyrothenic[1,2]. This composition undergoes a reaction which evolves high energy and a large amount of gas at high temperature. Thus, the composition called a "pyrolant" is a very interesting material for a fireworks engineers. The purpose of this report is to clarify the thermal reaction and the combustion of the magnesium - containing pyrolants using thermal analysis, analysis of combustion residues, burning rate measurements and visual observation of combustion of the pyrolant, which is a mixture of magnesium with oxidizing agents. For this purpose, ammonium nitrate, ammonium perchlorate and potassium nitrate were selected as the oxidizing agents.

Received on November 2, 1999

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2. Experimental

2.1 Materials

The magnesium used in this study was METAL M-1002 obtained from CERAC Inc., in the USA. Its particle size is 10.2μm and the purity is 99.5%. Ammonium perchlorate, ammonium nitrate and potassium nitrate were all reagent grade, and their particle sizes were about 150μm after pulverizing and sieving. Stearic acid (SA) of particle diameter <150μm was used as a promoter of the sustained combustion of the incombustible pyrolant.

The mixture of magnesium fuel with oxidizer (pyrolant) was prepared by using an ordinary ball-mill mixer after weighing the ingredients. The incombustible pyrolant was improved by adding stearic acid

as subsidiary fuel to make it combustible. Formulations of the pyrolants were determined according to equations (1)～(3) and are shown in Table 1.

$$5Mg + 2KNO_3 = N_2 + K_2O + 5MgO \quad (1)$$
$$5Mg + 2NH_4ClO_4 = N_2 + 3H_2O + 2HCl + 5MgO \quad (2)$$
$$Mg + NH_4NO_3 = N_2 + 2H_2O + MgO \quad (3)$$

2.2 Combustion experiments

The pyrolants were burnt in an aluminum cylindrical tube, and the time for 10mm burning was recorded using a Digital Stragescope from the Iwasaki Tuusinki Co., LTD. with optical fiber signals. The aluminum tube has inside diameter of 6mm, outside diameter of 15mm and 30mm length. One pyrolant composition divided into equal nine part was loaded nine times in one aluminum tube, and the bulk density was 70% of the theoretical maximum density. Measurement was carried out 5 times in atmospheric and pressurized nitrogen.

2.3 Analysis

Thermal analysis was performed using a RIGAKU DTA-TG simultaneous analyzer. The sample weight was 5mg and the heating rate was 20℃/min under an argon gas stream. The sample container was an open alumina crucible (5mm i.d.× 5mm height) for magnesium, potassium nitrate and their mixture, and a hermetically sealed aluminum crucible which had a pin hole in the center of the cover for ammonium nitrate, ammonium perchlorate and their mixture with magnesium.

A qualitative analysis of the reaction products was performed using common X-ray powder diffraction or a UV analyzer after dissolving the products in distilled water.

Observation of the reaction process on heating was carried out using an optical microscope which was attached to the heating apparatus LK-1500 from Japan Hightec Co., Ltd..

Table 1 Formulation of magnesium - oxidizing agent pyrolants

Mg/AN	Mg/PN	Mg/AP	O balance
30/70	43/57	40/60	− 10
28/72	40/60	37/63	− 5
23/77	38/62	34/66	0
18/82	34/66	30/70	+ 5
13/87	31/69	26/74	+ 10

AN ; NH_4NO_3, PN ; KNO_3, AP ; NH_4ClO_4, O balance ; oxygen balance

3. Results and discussion

3.1 The reaction of magnesium with potassium nitrate

Figure 1 shows the results of thermal analysis of magnesium in air, potassium nitrate in air and their mixture in argon. Magnesium was gradually oxidized at about 500℃ and underwent a vigorous exothermic reaction at 580℃. Because the melting point of magnesium is 600℃, magnesium is initially oxidized in the solid state in air. On heating, potassium nitrate undergoes melting at 340℃ and gradually decomposes in the temperature range of 620-1000℃. The weight decrease up to 1000℃ is 44.4%. Conkling and Stern et. al. stated that the thermal decomposition of potassium nitrate occurred according to the following equations (1)～(3)[3),4)] ;

$$2KNO_3 \rightarrow K_2O + N_2 + 2.5O_2 \quad (1)$$
$$2KNO_3 \rightarrow K_2O + 2NO_2 + 0.5O_2 \quad (2)$$
$$2KNO_3 \rightarrow K_2O + 2NO + 1.5O_2 \quad (3)$$

Stern also reported that an equilibrium of equation (4) existed between potassium nitrate, potassium nitrite and oxygen. In this experiment, potassium

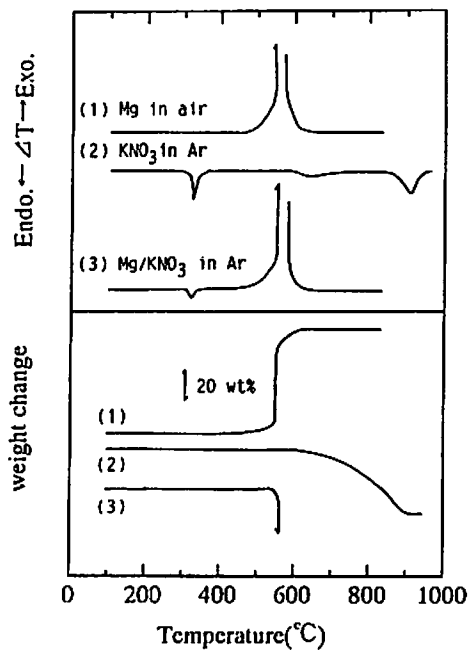

Fig. 1 DTA and TG curves of Mg (in air, 1), KNO_3 (Ar, 2) and their mixture (Ar, 3)

nitrite was also observed in the condensed phase in the potassium nitrate decomposition at 600℃.

$$KNO_3 = KNO_2 + 0.5O_2 \quad (4)$$

Because the product gases in the course of the decomposition were not analyzed, the exact decomposition equation could not be determined. However, the observed weight loss was in good agreement with the calculated loss based on the postulation of the reaction residue being potassium oxide (K_2O). At higher temperature, the reaction residue potassium oxide spilled out after creeping up the wall of the sample container and corroded the sample holder. Therefore, it is necessary to prevent damage to the apparatus caused by corrosion during the thermal analysis of potassium nitrate or its mixture.

The mixture of magnesium with potassium nitrate under atmospheric condition gradually underwent an exothermic reaction at about 450℃ and subsequently underwent a vigorous reaction with bright light production (Fig. 1-3). Because of severity of the reaction, the residue was scattered after the reaction. Figure 2 shows the results of thermal analysis of the various mixtures of magnesium with potassium nitrate under atmospheric and pressurized conditions. The reaction temperatures of the mixtures were almost all the same among the various compositions, indicating that the reaction was independent of the composition. Under pressurized condition, the mixture showed the same thermal behavior as that under atmospheric condition, indicating that pressure did not affect much.

Observation of the reaction process by an optical microscope showed that magnesium underwent swelling before the reaction, producing hollows in it, and that an intense reaction with bright light occurred just after the molten potassium nitrate spilled into the hollows. X-ray powder diffraction analyses of the reaction residue were carried out for magnesium in air and the mixture in argon at 600℃. Potassium magnesium oxide ($3K_2O \cdot MgO$) and potassium nitrite were confirmed as the reaction residue, but magnesium nitrate was not detected in the course of the reaction.

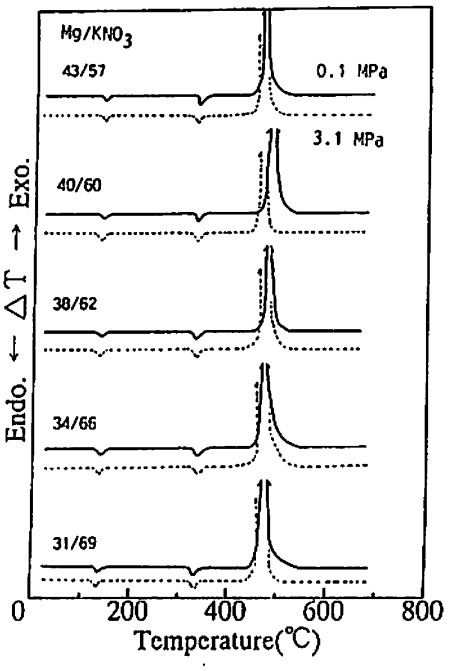

Fig. 2 Thermal analysis of the various mixtures of Mg with KNO_3 under atmospheric and pressurized conditions

The linear burning rate of magnesium - potassium nitrate pyrolants was measured under various pressures. The results are shown in Table 2 (and Figs. 7, 8). Under atmospheric pressure, the magnesium - potassium nitrate pyrolants had a linear burning rate of 4.38-14.36mm/min, and a maximum value of 14.36 mm/min was obtained for the stoichiometric composition. The burning rate of magnesium - potassium nitrate pyrolants was high compared to the other two pyrolants (the maximum value was six times that of the other two). Ordinarily, the maximum value of

Table 2 Linear burning rate of Mg - KNO_3 mixtures under atmospheric and pressurized conditions

wt%	0.1MPa	1.1MPa	3.1MPa	4.1MPa	n
31/69	4.38	13.43	20.40	30.07	0.488
38/62	14.36	37.05	60.10	66.73	0.414
43/57	5.32	15.91	25.03	43.23	0.516

the burning rate for pyrolants is obtained with a fuel-rich composition[3]. This is ascribed to the higher thermal conductivity or thermal diffusivity of the metal-rich composition. The burning rate of magnesium - potassium nitrate pyrolants increased with increasing ambient pressure up to 4.1MPa. In propellant combustion, the linear burning rate under pressurized conditions r is represented by the following Vieille equation:

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

where P is the pressure, n is the pressure exponent and b is a constant. The pressure exponent n was 0.49, 0.41 and 0.52 for magnesium/potassium nitrate = 31/69, 38/62 (stoichiometric composition) and 43/57 by weight, respectively.

3.2 The reaction of magnesium with ammonium perchlorate

Figure 3 shows the results of thermal analysis of ammonium perchlorate and its mixture with magnesium under atmospheric pressure and pressurized argon. Under atmospheric pressure, ammonium perchlorate underwent low-temperature decomposition at about 315℃ and the-high temperature decomposition at about 440℃[6]. Under pressurized condition, the low-temperature decomposition was restrained, and the reaction occurred at higher temperature with increasing pressure. On the other hand, a contrary pressure effect was recognized on the high-temperature reaction, and its reaction temperature became lower. Because of the contrary effect, both decomposition occurred at once above 3.0MPa. The reaction of the mixture of magnesium with ammonium perchlorate also occurred by steps ranging between 310-450℃ under atmospheric pressure. Under pressurized condition, the reaction occurred in one step, as in the case of ammonium perchlorate decomposition. However, the temperature at which the intense exothermic reaction commenced was nearly the same as that under atmospheric condition. Therefore, the reaction of the mixture was less affected by the surrounding pressure compared to the reaction of pure ammonium perchlorate.

Figure 4 shows the results of x-ray powder diffraction analysis of the reaction residue of the stoichiometric composition which was sampled at 430℃. Magnesium oxide and magnesium perchlorate were detected in the reaction residue (The x-ray analysis was carried out at room temperature after cooling the sample to room temperature : therefore, magnesium perchlorate may have become hydrated because of its high hygroscopicity).

Table 3 (and Figs. 7, 8) show the results of the linear burning rate measurements of magnesium - potassium nitrate pyrolants measured under various pressures. Under atmospheric pressure, the magnesium - ammonium perchlorate pyrolants had a linear burn-

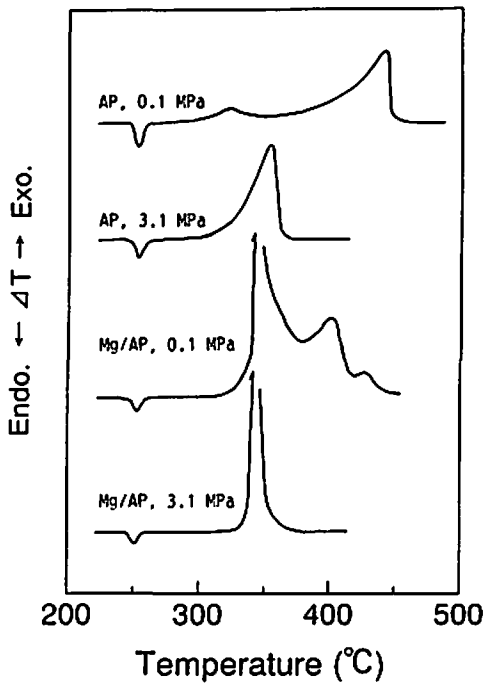

Fig. 3 DTA curves of the mixture of Mg with NH_4ClO_4 under atmospheric pressure and pressurized argon

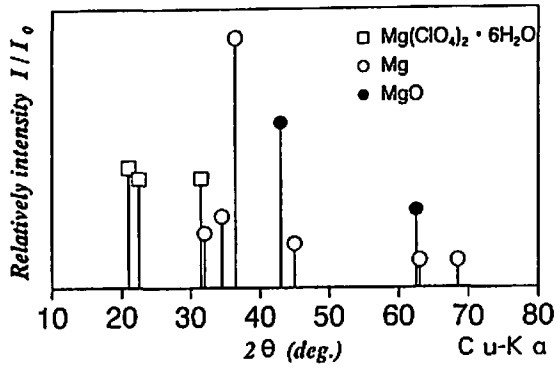

Fig. 4 X-ray powder diffraction analysis of the reaction residue of the stoichiometric mixtures of Mg with NH_4ClO_4 (at 430℃)

Table 3 Linear burning rate of Mg - NH_4ClO_4 mixtures under atmospheric and pressurized conditions

wt%	0.1MPa	1.1MPa	3.1MPa	4.1MPa	n
26/74	1.67	9.83	18.70	20.30	0.685
34/66	2.84	11.15	20.05	23.65	0.570
40/60	1.98	10.30	19.50	21.68	0.653

ing rate of 1.67-2.84mm/min and a maximum value of 2.84mm/min was obtained for the stoichiometric composition. The burning rate of magnesium - ammonium perchlorate pyrolants was smaller than that of the magnesium - potassium nitrate pyrolants. The burning rate of magnesium - ammonium perchlorate pyrolants under pressurized conditions also increased with increasing ambient pressure up to 4.1MPa. The pressure exponent was around 0.57-0.69, somewhat larger than that of the magnesium - potassium nitrate pyrolant.

3.3 The reaction of magnesium with ammonium nitrate

Figure 5 shows the results of thermal analysis of ammonium nitrate and its mixture with magnesium under atmospheric pressure and pressurized argon. In the DTA curves for ammonium nitrate under atmospheric pressure, there were three endotherms at about 128℃ ascribed to the transition, 170℃ to the melting and 225℃ relating to the evaporation; there was no exotherm. Under pressurized condition, the same endothermic peaks appeared below 200℃, while exotherms relating to decomposition could be found above 200℃.

The reaction of magnesium with ammonium nitrate exothermically occurred by steps under atmospheric pressure. The first exotherm appeared at 140℃ involving a large heat release and the second at 180-270℃. Under pressurized condition, an intense exothermic reaction occurred at 160℃ and was completed in one step. Therefore, because the temperature at which the intense exothermic reaction commenced is somewhat higher than that under atmospheric condition, the reaction of the mixture was restrained by the surrounding pressure, contrary to the reaction of the mixture of magnesium with ammonium perchlorate.

Figure 6 shows the results of x-ray powder diffraction analysis of the reaction residue of the stoichio-

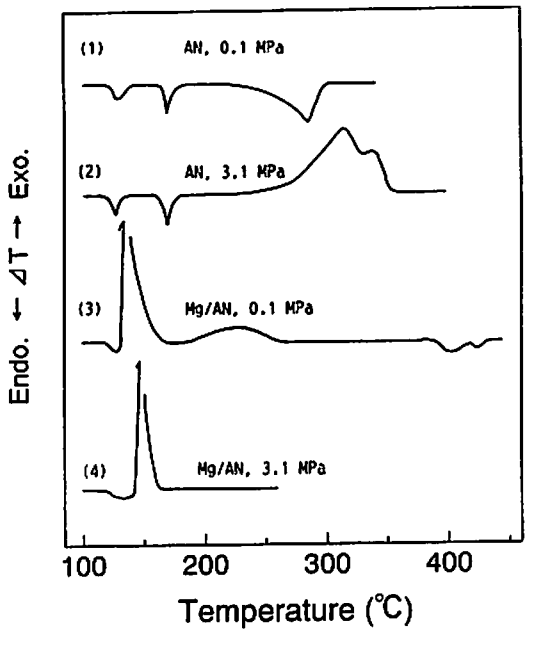

Fig. 5 DTA curves of the mixture of Mg with NH_4NO_3 under atmospheric pressure and pressurized argon

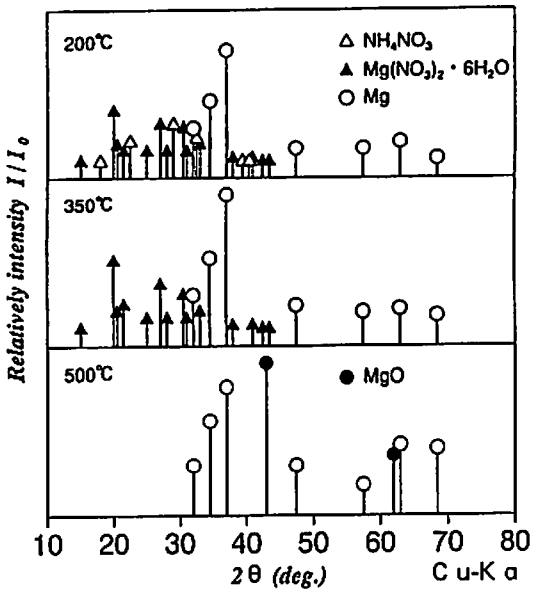

Fig. 6 X-ray powder diffraction analysis of the reaction residue of the stoichiometric mixture of Mg with NH_4NO_3

metric composition which was sampled at the temperature just after the end of the first step exothermic reaction in Fig. 5-3 (at about 200℃). Magnesium nitrate, unreacted magnesium and ammonium nitrate were detected (magnesium nitrate may have been hydrated because of its high hygroscopicity, as in the case of magnesium perchlorate). At 350℃, ammonium nitrate disappeared because of completion of decomposition. In the reaction residue at 500℃, magnesium oxide existed along with unreacted magnesium. Therefore, the intermediate magnesium nitrate disappeared, causing the decomposition or the oxidation of magnesium at between 300-500℃. Under pressurized condition, the reaction occurred in one step, as in the case of the reaction of ammonium perchlorate.

Table 4 (and Figs. 7, 8) show the results of the linear burning rate measurements of magnesium - ammonium nitrate pyrolants under various pressures. Under atmospheric pressure, the magnesium - ammonium nitrate pyrolants had a linear burning rate of 1.87- 2.93mm/min, and a maximum value of 2.93mm/min was obtained for the stoichiometric composition. The burning rate of magnesium - ammonium nitrate pyrolants and the ammonium perchlorate pyrolant was smaller than the burning rate of magnesium - potassium nitrate pyrolants. The burning rate of magnesium - ammonium nitrate pyrolants under pressurized conditions also increased with increasing ambient pressure up to 4.1MPa. The pressure exponent was 0.44-0.48 which was almost equal to that of the magnesium - potassium nitrate pyrolant.

3.4 Comparison of the thermal reactivity and burning characteristics of pyrolants

The main exothermic reaction of the magnesium - ammonium nitrate pyrolant under atmospheric pressure occurred at 140℃ and was restrained under pressurized condition. On the other hand, the main exothermic reaction of the magnesium - ammonium perchlorate pyrolant occurred at a relatively higher temperature of 320℃ compared to that of magnesium - ammonium nitrate pyrolant and was less affected by the surrounding pressure. The magnesium - potassium nitrate pyrolant underwent an exothermic reaction under atmospheric condition at the highest temperature of about 450℃ among the three reactions independent of the surrounding pressure. Thus, the thermal reactivity of the magnesium - containing pyrolant was very different with the species of the oxidizing agent.

Figures 7, 8 and 9 show the comparison of the linear burning rates of the three pylolants under various pressures. The linear burning rates of the magnesium - potassium nitrate under atmospheric pressure (and also pressurized condition) was about 6 times as fast as that of the magnesium - ammonium perchlorate or ammonium nitrate pyrolant. On the other hand, thermal analysis revealed that the magnesium - ammonium nitrate pyrolant was the most reactive and that the magnesium - potassium nitrate had the lowest

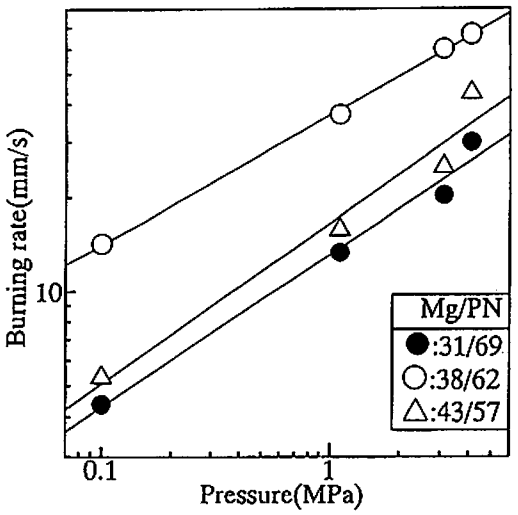

Fig. 7 Linear burning rate of magnesium - potassium nitrate pyrolants under different pressures

Table 4 Linear burning rate of Mg - NH_4NO_3 mixtures under atmospheric and pressurized conditions

wt%	0.1MPa	1.1MPa	3.1MPa	4.1MPa	n
13/87	1.87	3.36	8.66	9.32	0.443
23/77	2.93	9.07	13.26	15.38	0.443
30/70	1.96	6.73	9.64	11.84	0.475

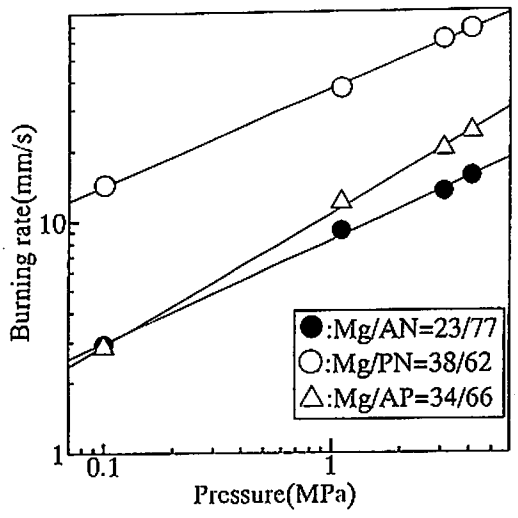

Fig. 8 Linear burning rate of magnesium - various oxidizing agent pyrolants under different pressures

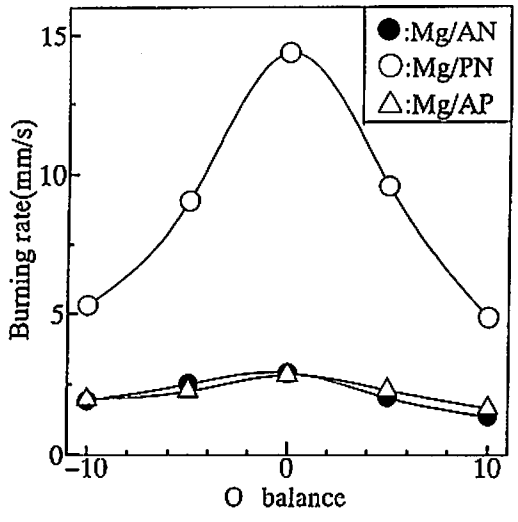

Fig. 9 Relationships between linear burning rate (under 0.1MPa) and oxygen balance for various pyrolants

reactivity. Therefore, there is no apparent relation between the thermal reactivity and the combustion among the three. What physical or chemical effect caused this phenomenon was not clarified in this experiment.

Analysis of the thermal reaction process revealed that the low burning rate pyrolant, magnesium - ammonium perchlorate or ammonium nitrate mixture, produced the intermediates of magnesium perchlorate or nitrate. These intermediates of magnesium nitrate and magnesium perchlorate were less reactive compared to the original ammonium nitrate and ammonium perchlorate. This may be one reason for the difference in combustion characteristics. However, because exact role of the intermediates in combustion has not been examined, the exact reason remains unclarified.

4. Conclusions

In this report, the thermal reaction and the combustion of magnesium - containing pyrolant, which are mixtures of magnesium with ammonium nitrate, ammonium perchlorate and potassium nitrate, were studied. With regard to the thermal reactivity, magnesium - ammonium nitrate pyrolant showed the highest reactivity and magnesium - potassium nitrate pyrolant the lowest. In the course of the reaction, the pyrolants of magnesium - ammonium nitrate or ammonium perchlorate produced intermediates of magnesium nitrate or perchlorate, but none of the intermediate was found with the magnesium - potassium nitrate pyrolant.

The combustion characteristics of the pyrolants were different with the species of oxidizing agent, ambient pressure and the composition. As the oxidizing agent, potassium nitrate had a linear burning rate about six times larger than that of the others under any ambient pressure. The linear burning rate of the pyrolants increased with increasing ambient pressure. The magnesium - ammonium nitrate and potassium nitrate pyrolants had approximately the same pressure exponent of 0.41-0.52 and the ammonium perchlorate pyrolant had a slightly larger value. Maximum burning rates of these pyrolants were obtained for the stoichiometric composition.

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マグネシウム－酸化剤系パイロラントの反応性

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パイロラントとは金属と酸化剤から成る組成物で，推進薬と火工品の両方の機能を持つ燃焼系と桑原らによって定義されている。これらは，高エネルギーと高温のガスを同時に生成する所に特徴がある。本研究では，このパイロラントの熱反応および燃焼反応を，熱分析，燃焼残留物の分析，燃焼状態の観察および燃焼試験などによって検討した。パイロラントとしては，マグネシウム－硝酸カリウム，過塩素酸アンモニウム，硝酸アンモニウム系を選んだ。

マグネシウムを含むパイロラントの反応性は酸化剤の種類により異なった。マグネシウム－硝酸アンモニウムパイロラントは熱的には最も活性で，マグネシウム－硝酸カリウムパイロラントはこの三者では最も不活性であった。しかし，マグネシウム－硝酸カリウムパイロラントの燃焼速度はマグネシウム－過塩素酸アンモニウムや硝酸アンモニウム系の数倍であり，熱反応性と燃焼反応性との間には見かけ上の相関性がなかった。

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