Effect of catalysts on the reactivity of ammonium perchlorate-sodium nitrate-aluminum- GAP composite solid propellant

Hidetsugu NAKAMURA*, Kenzi YOSHIHIRA*, Miyako AKIYOSHI*, and Yasutake HARA*

The thermal reaction and the combustion of an ammonium perchlorate(AP)-sodium nitrate(SN)-aluminum(Al)-GAP-catalyst solid propellant were studied by a thermal analysis, combustion experiments and analyses of the reaction residue in order to clarify the catalytic effect of iron oxide, copper oxide and cobalt oxide catalysts. The results obtained are as follows.

Iron oxide, which has a catalytic effect on ammonium perchlorate and a AP-Al-GAP solid propellant decomposition, had no effect on the thermal reaction of the mixture of ammonium perchlorate with sodium nitrate and the AP-SN-Al-GAP solid propellant. Cobalt oxide and copper oxide had a catalytic effect on the low temperature decomposition of ammonium perchlorate in the mixture of ammonium perchlorate and sodium nitrate at atmospheric pressure, but had no effect on the thermal reaction of the AP-SN-Al-GAP solid propellant under pressurized conditions.

With regard to the combustion, iron oxide had no catalytic effect on the AP-SN-Al-GAP composite solid propellant. The formation of sodium perchlorate, which is more stable compared to ammonium perchlorate, is one of the reason for this phenomenon. The addition of a copper oxide catalyst increased the burning rate by 5～15% compared to that without a catalyst, but cobalt oxide showed no catalytic effect on a sodium nitate containing propellant combustion under pressurized conditions.

1. Introduction

Ammonium perchlorate has been mainly used as an oxidizer in practical solid rocket propellants. However, it has the problem of producing acid rain over the launching district and ozone destruction in the stratosphere due to hydrochloric acid production. An ammonium perchlorate (AP, NH_4ClO_4) – sodium nitrate (SN,$NaNO_3$) – aluminum (Al) – glysidyl azide polymer(GAP) composite solid propellant (abbreviated as AP-SN-Al-GAP propellant) is one of the candidates for a chlorine-free non-polluting solid propellant. Though the thermal reaction and combustion of these types of propellants have been studied by some workers[1)~3)], there are few reports which evaluated a catalyst for this propellants.

An iron containing catalyst such as iron oxide or catocene was a famous combustion catalyst of an aluminized ammonium perchlorate composite solid propellant. But, there has been no study of whether or not these catalysts have an effect on an AP-SN-Al-GAP propellant. In this paper, the effect of iron oxide, copper oxide and cobalt oxide catalysts on the thermal reaction and the combustion of the AP-SN-Al-GAP propellant were studied by thermal analysis, combustion experiments and analyses of the reaction residue.

Received on November 11, 1999

*Department of Applied Chemistry, Faculty of Engineering, Kyushu Institute of Technology, Sensui, Tobata, Kitakyushu, 804-8550 JAPAN
TEL 093－884－3319
FAX 093－884－3308

2. Experimental

2.1 Materials

The aluminum used in this study was obtained from Alcoa, Inc., in the USA. Its particle size is below 5 μm and the purity is 99.5 %. Ammonium perchlorate and sodium nitrate were reagent grade, and their particle sizes were about 150 μm after pulverizing and sieving. The iron oxide catalyst(α-Fe_2O_3) was obtained from Tohoganry-ou K.K. and its particle size is about 0.2 μm. Copper oxide(CuO) and cobalt oxide(Co_3O_4), having average particle diameters of about 5 μm and 4 μm, respectively, were reagent grade and used without processing such as thermal treatment or pulverization. Ten types of propellants were prepared using 20.0 wt.% GAP as the binder, 62.4 wt.% oxidizer and 17.6 wt.% aluminum, and 0~5 wt.% catalysts were added to the propellants. The formulations are listed in Table 1.

2. 2 Analysis

Thermal analyses were 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. The sample container was an open alumina crucible (5mm i.d×5mm height).

A qualitative analysis of the reaction products was performed using X- ray powder diffraction.

2. 3 Combustion experiment

The linear burning rate was measured for the strands formed in a 6mm × 6mm shape. The time needed for the 40 mm burning of the strands was measured by means of a chimney type strand burner under pressurized nitrogen ranging from 3 to 10 MPa.

3. Results and discussion

3. 1 Effect of the catalyst on the decomposition of ammonium perchlorate and the mixture of ammonium perchlorate with sodium nitrate

Fig.1 (2) shows the results of the thermal analysis of ammonium perchlorate and the mixture of ammonium perchlorate with sodium nitrate in air. Ammonium perchlorate underwent a transition at 230℃, a low temperature decomposition at about 300℃ and a high temperature one at 440℃ with a vigorous heat release. The DTA trace of the mixture of ammonium perchlorate with sodium nitrate showed two exotherms at 300℃ and 560℃, and an endotherm at 455℃. X- ray powder diffraction analyses of the reaction residue were carried out at 360 and 650℃. The reaction residue at 360℃ was sodium perchlorate and that at 650℃ was sodium chloride (Fig.2). The observed weight loss of 41% corresponded well to the calculated one of 40% according to equation (1), in which ammonium nitrate formed was assumed to decompose and gasify:

$$NH_4ClO_4 + NaNO_3 \rightarrow NaClO_4 + NH_4NO_3 \qquad (1)$$

Table 1 Formulations of NH_4ClO_4-$NaNO_3$-GAP-Al-catalyst composite solid propellant

	GAP	AP	SN	Al	Fe_2O_3	CuO	Co_3O_4
No.1	20	62.4	−	17.6	−	−	−
No.2	20	62.4	−	17.6	2.5	−	−
No.3	20	62.4	−	17.6	5.0	−	−
No.4	20	36.0	26.4	17.6	−	−	−
No.5	20	36.0	26.4	17.6	2.5	−	−
No.6	20	36.0	26.4	17.6	5.0	−	−
No.7	20	36.0	26.4	17.6	−	2.5	−
No.8	20	36.0	26.4	17.6	−	5.0	−
No.9	20	36.0	26.4	17.6	−	−	2.5
No.10	20	36.0	26.4	17.6	−	−	5.0

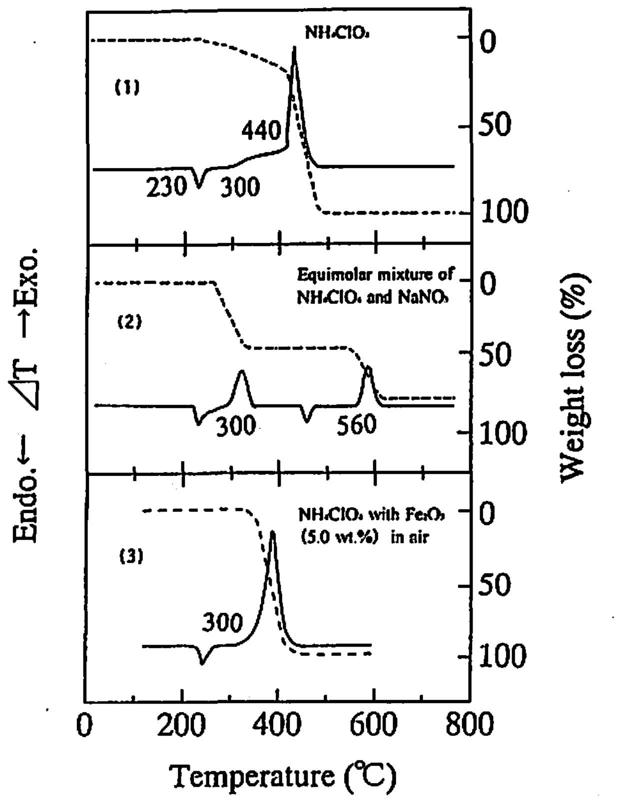

Fig. 1 DTA and TG curves of NH_4ClO_4, the mixture of NH_4ClO_4 with $NaNO_3$ and NH_4ClO_4 with iron catalyst in air

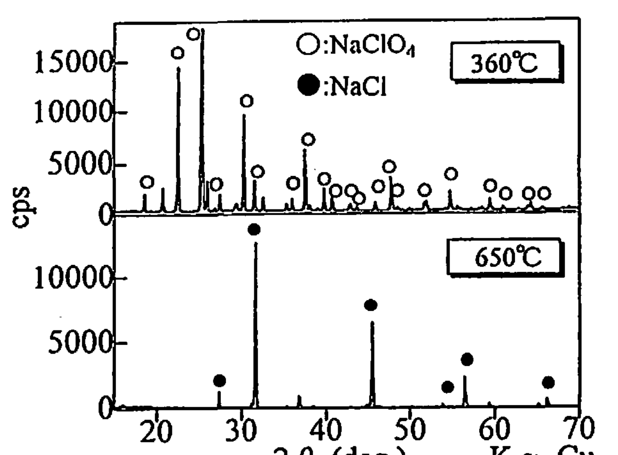

Fig. 2 X-ray powder diffraction analysis of the reaction residue of the stoichiometric mixture of NH_4ClO_4 with $NaNO_3$

This double decomposition was confirmed by the fact that the observed endotherm at 455℃, which was accompanied by no weight change, corresponded to the melting point of the formed sodium perchlorate[4]. The observed final weight remaining of 27% was in good agreement with the calculated value of the sodium chloride formation described by equation (2):

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

Fig.1 (3) shows the results of the thermal analysis of ammonium perchlorate with 5wt. % iron oxide catalyst added. Unlike the case without a catalyst in which a two-step decomposition occurred, ammonium perchlorate with the iron oxide catalyst underwent an intense decomposition at 300℃.

Fig.3 shows the results of the thermal analysis of a binary mixture of ammonium perchlorate and sodium nitrate, and ternary mixtures of ammonium perchlorate, sodium nitrate and catalysts, in which the catalyst level was 5wt. % of the total amount of ammonium perchlorate and sodium nitrate. The ternary mixtures of ammonium perchlorate, sodium nitrate and iron oxide catalysts showed the same DTA trace as the mixture of ammonium perchlorate with sodium nitrate, and iron oxide has no catalytic effect on the ammonium perchlorate in the mixture. On the other hand, the DTA trace of the ternary mixtures of ammonium perchlorate, sodium nitrate and the copper oxide catalyst showed an intense exotherm at 290℃ that corresponded to the low temperature decomposition, an endotherm at 425℃ and a small exotherm at 490℃. When cobalt oxide was added to the mixture, the DTA trace of the ternary mixtures showed an intense exotherm at 280℃ that orresponded to the low temperature decomposition, an endotherm at 400℃ and a small exotherm at 415℃. Contrary to the iron oxide catalyst, both had a catalytic effect on the low temperature decomposition of ammonium perchlorate in the mixture. But, in these experiments, the reaction intermediate and the final exothermic decomposition products that occurred were not studied for the mixture with copper oxide and cobalt oxide catalysts.

Fig.4 shows the results of the thermal analysis of a AP-Al-GAP propellant with iron oxide catalyst and a AP-SN-Al-GAP propellant with iron oxide catalyst under pressurized argon in which the catalyst levels were from 0 to 5 wt. % of the total amount of oxidizer. Under pressurized conditions, the AP-Al-GAP propellant without iron oxide catalyst underwent an intense exothermic decomposition at 250 ℃. This

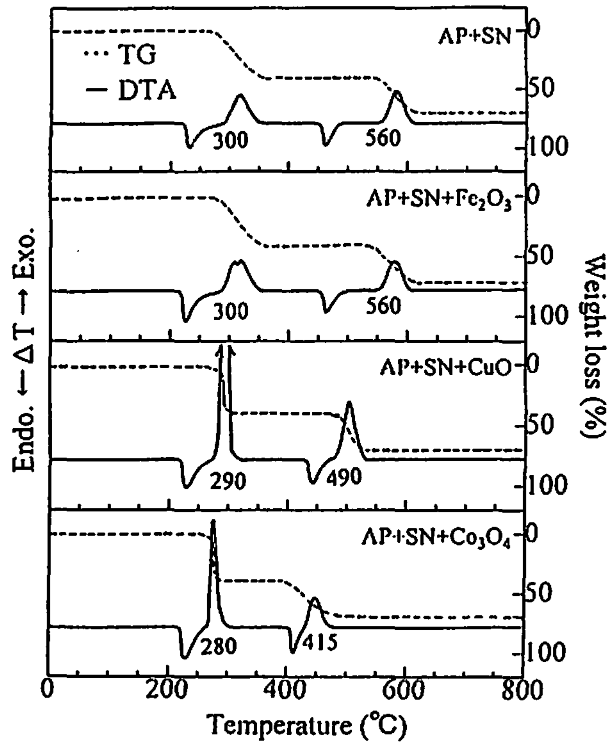

Fig. 3 Thermal analysis of a binary mixture of NH_4ClO_4 and $NaNO_3$, and ternary mixtures of NH_4ClO_4, $NaNO_3$ and catalysts (5wt. %) in air

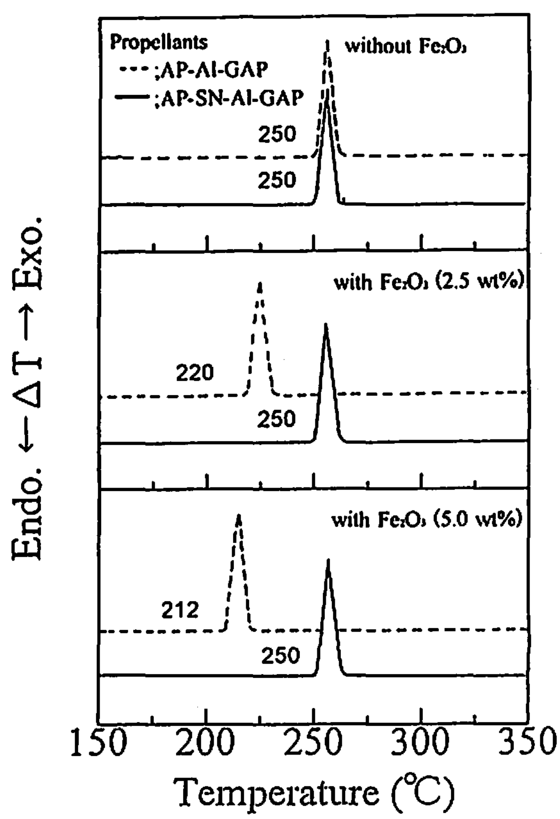

Fig. 4 Effect of the iron oxide catalyst on the thermal reactivity of NH_4ClO_4-Al-GAP and NH_4ClO_4-$NaNO_3$-Al-GAP composite solid propellants under pressurized argon (5.1 MPa)

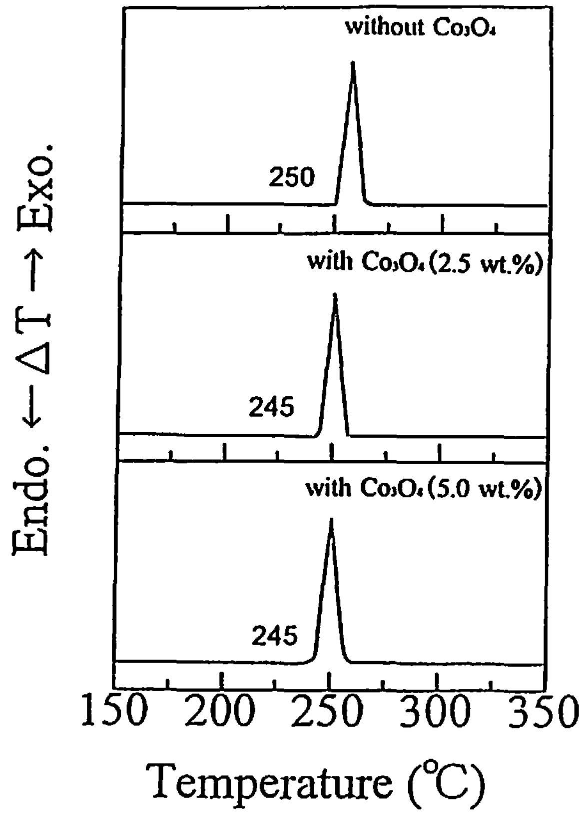

Fig. 5 Effect of the cobalt oxide catalyst on the thermal reactivity of NH_4ClO_4-$NaNO_3$-Al-GAP composite solid propellant under pressurized argon (5.1 MPa)

decomposition temperature decreased with increasing catalyst level. The AP-SN-Al-GAP propellant with and without iron oxide catalyst also showed an intense exothermic decomposition at 250℃, but the catalytic effect of iron oxide was not recognized.

Fig.5 shows the effect of the cobalt oxide catalyst on the thermal reactivity of the AP-SN-Al-GAP propellant under pressurized argon in which the catalyst levels were from 0 to 5 wt. % of the total amount of oxidizer. Under pressurized conditions, the AP-SN-Al-GAP propellant with and without cobalt oxide catalyst underwent an intense exothermic decomposition at 250 ℃. However, the propellant with cobalt oxide catalyst had the same decomposition temperature as that without the catalyst and no catalytic effect was recognized. With regard to copper oxide, the AP-SN-Al-GAP propellant with a catalyst had the same decomposition temperature as that without a catalyst (Fig.6) and no catalytic effect was again recognized under pressurized conditions.

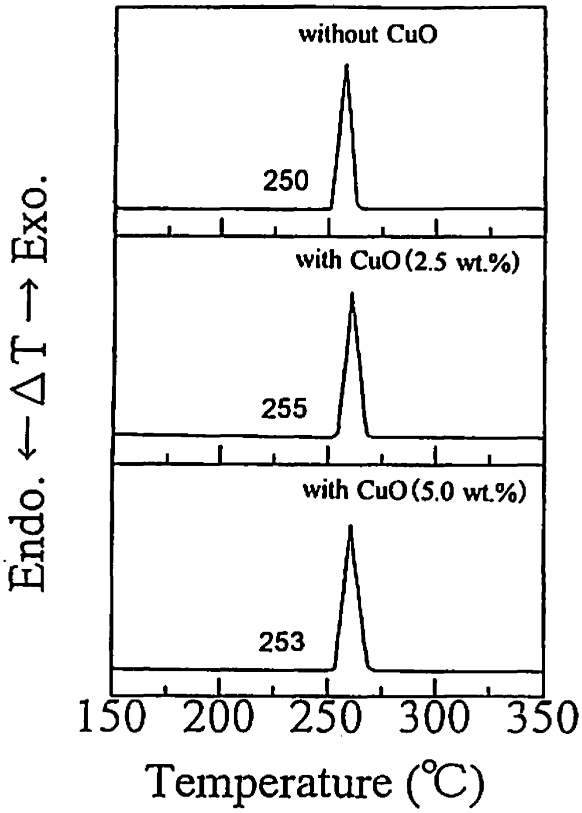

Fig. 6 Effect of the copper oxide catalyst on the thermal reactivity of NH_4ClO_4-$NaNO_3$-Al-GAP composite solid propellant under pressurized argon (5.1 MPa)

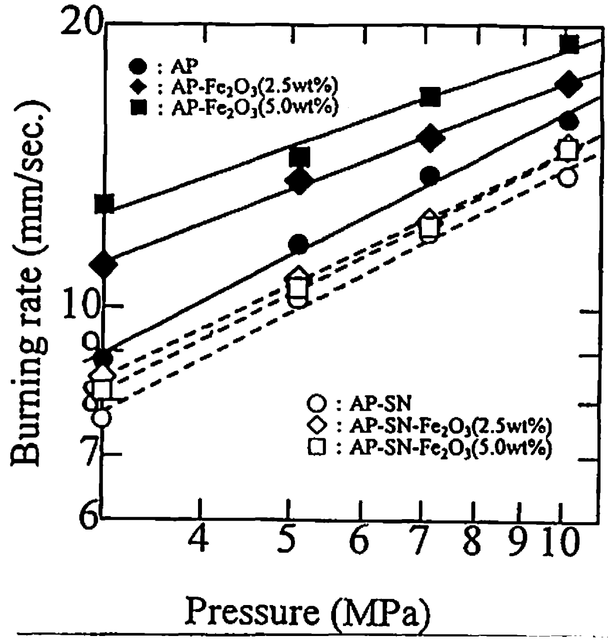

Fig. 7 Effect of iron oxide catalyst on linear burning rate of NH_4ClO_4-Al-GAP and NH_4ClO_4-$NaNO_3$-Al-GAP composite solid propellants under pressurized nitrogen

3. 2 Effect of the catalyst on the combustion of an ammonium perchlorate – aluminum – GAP and an ammonium perchlorate – sodium nitrate – aluminum – GAP composite solid propellant

Fig. 7 shows the results of the linear burning rate measurements for an ammonium perchlorate – aluminum – GAP polymer – iron oxide catalyst and an ammonium perchlorate – sodium nitrate – aluminum (Al) – glysidyl azide polymer (GAP) – iron oxide catalyst composite solid propellant (abbreviated as a sodium nitrate-containing propellant) under pressurized nitrogen, in which the catalyst level was from 0 to 5wt. % of the total amount of propellant. The linear burning rate of an ammonium perchlorate – aluminum – GAP polymer composite solid propellant increased with increasing amount of additive level and ambient pressure. On the other hand, the effect of iron catalysts on the combustion of the sodium nitrate-containing propellant was different from that without sodium nitrate; that is, the linear burning rate of a sodium nitrate- containing propellant increased with ambient pressure, but did not change with an increasing amount of additive.

Iron oxide is a well-known catalyst for ammonium perchlorate and ammonium perchlorate containing propellants. However, it has no effect on the decomposition of the mixture of ammonium perchlorate with sodium nitrate and a sodium nitrate-containing propellant. In this experiment, a detailed investigation was not carried out, but the mixture of ammonium perchlorate with sodium nitrate did produce a sodium perchlorate intermediate. This intermediate was less reactive compared to the original ammonium perchlorate. This may be one reason for the difference in the combustion characteristics between a sodium nitrate- containing propellant and that without sodium nitrate.

In propellant combustion, the linear burning rate under pressurized conditions V is represented by Vieille's equation (3):

$$V = b P^n \quad (3)$$

where P is the pressure, n is the pressure index and b is a constant. The pressure index n for the ammonium perchlorate – aluminum – GAP propellant without a catalyst, with 2.5wt.% and 5wt. % catalyst were 0.51, 0.40 and 0.33,

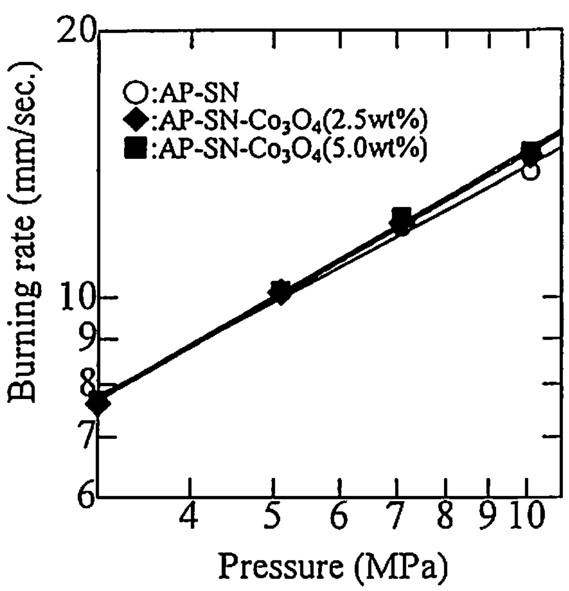

Fig. 8 Effect of cobalt oxide catalyst on linear burning rate of NH_4ClO_4-$NaNO_3$-Al-GAP composite solid propellant under pressurized nitrogen

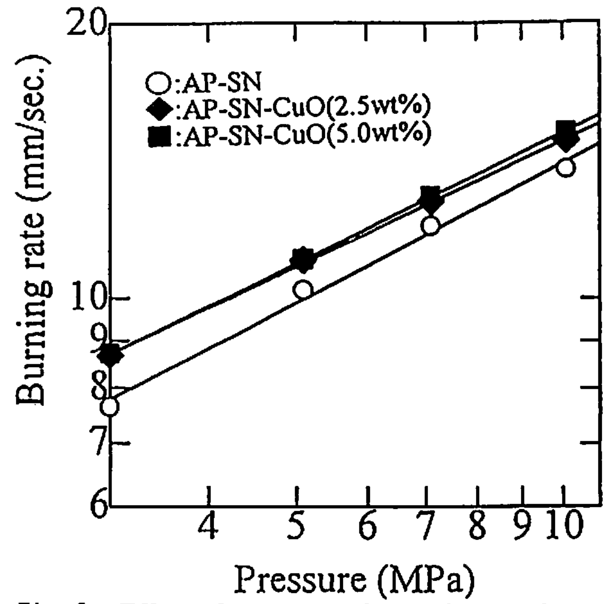

Fig. 9 Effect of copper oxide catalyst on linear burning rate of NH_4ClO_4-$NaNO_3$-GAP-Al composite solid propellant under pressurized nitrogen

respectively, and decreased with increasing catalyst level. However, the pressure index n of a sodium nitrate – containing propellant is approximately the same value of 0.47～0.50.

Fig. 8 shows the effect of cobalt oxide on the linear burning rate of a sodium nitrate containing propellant under a pressurized condition of nitrogen, in which the catalyst levels were from 0 to 5 wt. % of the total amount of propellant. The linear burning rate of a sodium nitrate-containing propellant increased with increasing ambient pressure, but did not change with increasing additive level of the cobalt oxide catalyst. Moreover, the pressure index also had the same value of 0.50～0.54 for the different catalyst levels.

Fig. 9 shows the effect of copper oxide catalyst on the linear burning rate of a sodium nitrate-containing propellant under pressurized nitrogen, in which the catalyst levels were from 0 to 5 wt. % of the total amount of propellant. The linear burning rate of a sodium nitrate-containing propellant increased with increasing ambient pres sure and showed an increase of 5～15% compared to that without a catalyst. The pressure index also had the same value of 0.45～0.50 for the different catalyst levels.

4. Conclusions

This experiment was carried out in order to clarify the catalytic effect of some metallic oxide catalysts on the thermal decomposition of the mixture of ammonium perchlorate with sodium nitrate and an AP-SN-Al-GAP composite solid propellant. With regard to the thermal reaction, iron oxide, which has a catalytic effect on the ammonium perchlorate decomposition and the AP-Al-GAP propellant decomposition, had no effect on the thermal reaction of the AP-SN-Al-GAP propellant. Cobalt oxide and copper oxide had a catalytic effect on the low temperature decomposition of ammonium perchlorate in the mixture of ammonium perchlorate with sodium nitrate under atmospheric pressure, but had no effect on the thermal reaction of the AP-SN-Al-GAP propellant under pressurized conditions.

Iron oxide had no catalytic effect on the combustion of an AP-SN-Al-GAP composite solid propellant in contrast with the high activity during the combustion of an AP-Al-GAP composite solid propellant. The formation of sodium perchlorate, which is more stable than ammonium perchlorate during the course of the reaction of a sodium nitrate-containing propellant is considered to be one of the reasons of this phenomenon. Cobalt oxide showed no catalytic effect on a sodium nitate containing propellant under pressurized conditions. The addition of a copper oxide catalyst increased the burning rate by 5～15% compared to that without a catalyst.

References

1) K. Nozoe, Y. Azuma, T. Yamaya, M. Shimoda, H. Habu, K. Hori and T. Saito, The Proceedings of Autumn Meeting of Explosive Society of Japan (1999) p109

2) Y. TAKISHITA, T. ONDA, Y. TAKEI and C. TOHARA, J. of Japan. Explo. Soc., 60(2), 76(1999)

3) K. Yoshihira, K. Kobayashi, M. Akiyoshi, H. Nakamura and Y. Hara, The Proceedings of Spring Meeting of Explosive Society of Japan (1997) p109

4) F. Solymosi, "Structure and stability of salts of halogen oxy acids in the solid phase", John Wiley & Sons (1977) p126

過塩素酸アンモニウム－硝酸ナトリウム－アルミニウム－GAP系固体推進薬の反応性に及ぼす触媒の効果

中村英嗣*，吉平研司*，秋吉美也子*，原　泰毅*

過塩素酸アンモニウム－硝酸ナトリウムの混合物および過塩素酸アンモニウム－硝酸ナトリウム－アルミニウム－GAP系固体推進薬の熱反応性および燃焼反応性に及ぼす金属酸化物触媒の効果を，熱分析法，燃焼残留物の分析および燃焼実験などにより検討した。

過塩素酸アンモニウム単独の熱分解触媒である酸化鉄は，過塩素酸アンモニウムと硝酸ナトリウム混合物および過塩素酸アンモニウム－硝酸ナトリウム－アルミニウム－GAP系固体推進薬の熱反応には触媒効果を持たなかった。酸化コバルトと酸化銅は過塩素酸アンモニウムと硝酸ナトリウム混合物の常圧下での低温分解には触媒効果を示したが，加圧下での過塩素酸アンモニウム－硝酸ナトリウム－アルミニウム－GAP系固体推進薬の熱反応には効果を持たなかった。

酸化鉄は過塩素酸アンモニウム－硝酸ナトリウム－アルミニウム－GAP系固体推進薬の燃焼にも触媒効果を持たなかった。これは反応過程で過塩素酸アンモニウムよりも安定な過塩素酸ナトリウムの生成によると推定された。酸化コバルトは硝酸ナトリウムを含む推進薬の燃焼には触媒効果を持たなかった。酸化銅は硝酸ナトリウムを含む推進薬の燃焼速度を5～15%増加させ，若干の触媒効果を示した。

(*九州工業大学・工学部・応用化学教室　〒804-8550 北九州市戸畑区仙水町1－1)