Article

Burning characteristics of fuel-rich AP/HTPB composite propellant added with iron oxide

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Hybrid rocket motor has been developing for a rocket motor of the next generation. It is necessary to investigate the burning characteristics of fuel-rich AP/HTPB composite propellant in order to develop a solid fuel for hybrid rocket motor. Iron oxide is used as a positive catalyst for the AP/HTPB composite propellant. The burning characteristics of fuel-rich AP/HTPB composite propellant added with iron oxide were investigated in this study. From this study the following conclusions were obtained: 1) The burning rate decreases as the AP content decreases, and the propellants self-quench less than a certain AP content. The self-quenched combustion occurs at a lower pressure and a higher pressure. 2) The possibility of combustion for fuel-rich AP/HTPB composite propellant added with iron oxide is dependent on the AP content, the particle size of AP and the pressure. 3) The lower limit of AP content to combust is decreased by the addition of iron oxide. 4) The effect of the addition of iron oxide on the decrease in the lower limit of AP content to combust becomes greater as the size of AP particle decreases. 5) The effect of iron oxide on the increase in the burning rate is dependent on the AP content and the size of AP particle.

1. Introduction

Hybrid rocket motors have been developing for a rocket motor of the next generation. Gas hybrid rocket motor is a kind of hybrid rocket motors. Ammonium perchlorate (AP)/Hydroxyl terminated polybutadiene (HTPB) composite propellant is used as a solid fuel most widely. The burning characteristics of furl-rich AP/HTPB composite propellant have been investigating to develop a solid fuel of hybrid rocket.

The burning characteristics and the self-quenched combustion mechanism of fuel-rich AP/HTPB composite propellant were investigated in the previous paper[1]. It was found that the lower limit of AP content to combust, ϕ_{min} exists and ϕ_{min} of the propellant prepared with coarse AP is lower than that of the propellant prepared with fine AP. If ϕ_{min} could be decreased, the applicable field of a fuel-rich AP/HTPB propellant could be extended and, further, the amount of hydrogen chloride in combustion gases could be reduced. A fuel-rich AP/HTPB propellant at lower AP content is required in order to make a more wide useful of this propellant.

Iron oxide is known as a positive catalyst for the AP/HTPB composite propellant. It was expected that ϕ_{min} would be decreased by the addition of iron oxide to the propellant. The burning characteristics of fuel-rich AP/HTPB composite propellant added with iron oxide were investigated in this study. Detail on this experiment is reported in this paper.

2. Experiment

In this study coarse AP (CAP) and fine AP (FAP) were used as oxidizer in a similar to the previous study[1]. CAP was prepared by grinding a commercial AP for 5 minutes in a vibration ball mill. FAP was prepared by the freeze-drying method[2]. The shape of AP samples used in this study was almost spherical. The mean particle diameters of CAP and FAP were about 110 μm and 4 μm, respectively. Iron(Ⅲ) oxide was used as a burning rate catalyst. Iron oxide was added to 1 wt% of propellant[3]. HTPB was used as a binder. HTPB was cured with isophorone diisocyanate. Isophorone diisocyanate was added to 8 wt% of HTPB. The propellant mixtures were cured for 4 days at 333 K.

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Three lots of propellants were prepared at same AP content.

Thermochemical behavior of propellant was investigated by differentical thermal analysis (DTA) and thermogravimetry (TG). DTA and TG were carried out using a Rigaku TAS-100 Thermal Analyzier. The equipments were operated in a nitrogen flow condition at atmospheric pressure. The sample containers for the equipment were made of aluminium. The heating rate was 20 K/min.

The size of each strand was 10 mm × 10 mm in cross section and 40 mm in length. The side of each strand was inhibited by silicon resin. The burning rate was measured in a chimney-type strand burner which was pressurized with nitrogen. The strand burner was set in a temperature conditioner which is operated at a temperature of 288±1.5 K. The ignition of each strand was conducted by an electrically heated nichrome wire attached on the top of each strand. The propellant strand was combusted in pressure range of 0.5 MPa - 7 MPa. The burning phenomenon of the propellant was recorded with the high-speed video recorder. The burning rate was measured by the picture recorded with the high-speed video recorder. Three lots of propellants were prepared at same AP content as mentioned above. It is judged that the propellant cannot combust when one in the three lots of propellants was self-quenched or unignited.

3. Results and Discussion

3. 1 Thermochemical behavior

Thermochemical behavior of propellant contained at ϕ_{min} was investigated by DTA-TG. Figure 1 shows the DTA-TG curves of the propellants. For the propellant contained at 55 wt% CAP, a exothermic decomposition begins after the crystal transition point of AP and the peak of the exothermic decomposition of the propellant is shifted to 15 K lower by iron oxide. The decomposition rate of the propellant with iron oxide is a little higher than that of the propellant without iron oxide. The terminal weight loss of the propellant with iron oxide is approximately 7 wt% larger than that of the propellant without iron oxide.

For the propellant contained at 63 wt% FAP, the peak of the exothermic decomposition of the propellant is shifted to 91 K lower by iron oxide. The endothermic peak of the crystal transition point of AP is very small according to the DTA curve of the propellant with iron oxide because the shifting amount of the exothermic decomposition is large. The beginning temperature of decomposition is decreased approximately 20 K. The decomposition rate of the propellant with iron oxide is higher than that of the propellant without iron oxide.

These results show iron oxide makes the main decomposition region to shift to lower temperature. The

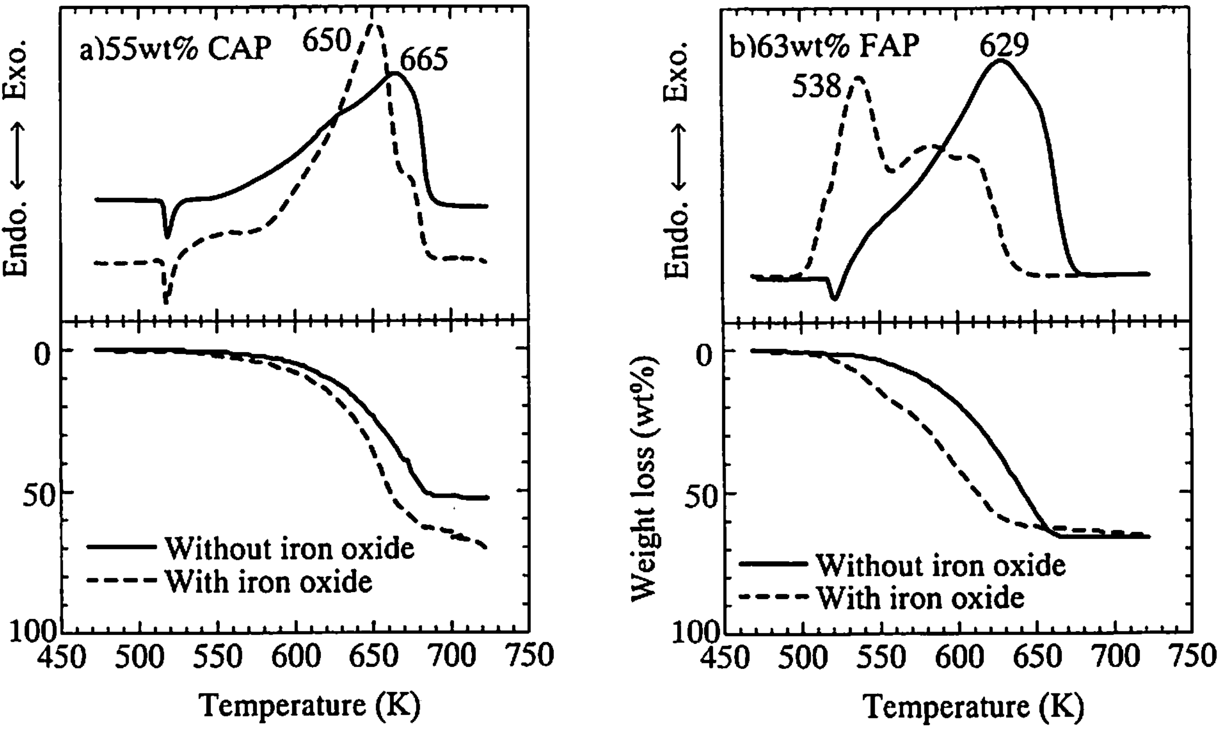

Fig.1 DTA-TG curves

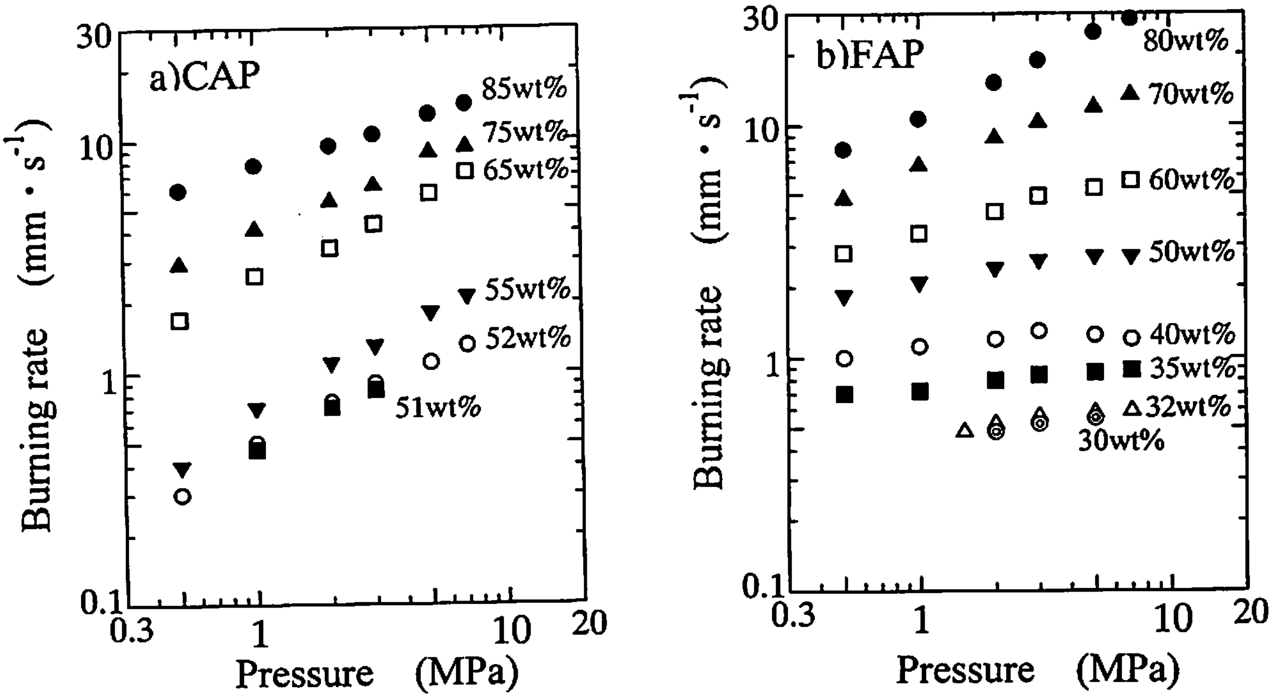

Fig.2 Burning rate characteristics

burning rate can be increased by shifting the main decomposition region of the propellant to lower temperature4). It can be supposed that ϕ_{min} could be decreased by the addition of iron oxide.

3. 2 Burning rate characteristics

Because of the requirements for the preparation of AP/HTPB composite propellant, the upper limit of AP content in propellant exists5)6). The upper limits of AP content in propellants prepared with FAP and CAP are 80 wt% AP and 85 wt% AP, respectively5)6). The propellant samples were prepared less than the upper limit of AP content in propellant with each AP sample. The burning rates of the propellants were measured. As mentioned in section 2, three lots of propellants were prepared at same AP content. It is judged that the propellant cannot combust when one in the three lots of propellants was self-quenched or unignited. The burning rate characteristics of the propellants are shown in Fig.2. The burning rate decreases as the AP content decreases. In regard to the propellant prepared with CAP, the propellants contained above 52 wt% AP combust, and that contained at 51 wt% AP combusts only between 1 MPa and 3 MPa. The propellants contained less than 51 wt% AP do not combust in the pressure range adopted in this study, between 0.5 MPa and 7 MPa. The linear plot of ln(burning rate) against ln(pressure) becomes a curved slope slightly as the AP content decreases. The overall pressure exponent in the pressure range of 0.5 MPa and 7 MPa cannot be calculated. As mentioned above, the propellant contained at 51 wt% AP combusts only between 1 MPa and 3 MPa. The pressure exponent in the vicinity of 2 MPa was calculated and the results are shown in Table 1. The range of the pressure exponent is from 0.35 to 0.45. It is found that

Table 1 Pressure exponent of propellant

AP content (wt %)	Pressure exponent (−)	
	CAP	FAP
85	0.35	−
80	−	0.49
75	0.39	−
70	−	0.38
65	0.34	−
60	−	0.28
55	0.40	−
52	0.45	−
51	0.41	−
50	−	0.15
40	−	0.14
35	−	0.13
32	−	0.27
30	−	0.63

the pressure exponent is almost constant in the case of the propellant prepared with CAP.

In regard to the propellant prepared with FAP, the propellants contained above 35 wt% AP combust between 0.5 MPa and 7 MPa. The propellant contained at 30 wt% AP combusts only between 2 MPa and 5 MPa. The propellants contained less than 29 wt% AP do not combust in the pressure range adopted in this study. The linear plot of ln (burning rate) against ln (pressure) becomes a curved slope slightly as the AP content decreases. The tendency is the same as that of the propellant prepared with CAP. The pressure exponent in the vicinity of 2 MPa was calculated in the same manner as the case of the propellant prepared with CAP. The results are also shown in Table 1. The pressure exponent decreases above 35 wt% AP and increases below that as AP content decreases.

The ϕ_{min} of the propellant with iron oxide was expressed as $c\phi_{min}$ in this study. According to their burning rate characteristics, $c\phi_{min}$ of CAP and FAP is 51 wt% AP and 30 wt% AP, respectively. This indicates that $c\phi_{min}$ of fine AP is lower than that of coarse AP. The self-quenched combustion occurs at a lower pressure and higher pressure. It is found that the possibility of combustion for fuel-rich AP/HTPB composite propellant added with iron oxide is dependent on the AP content, the particle size of AP and the pressure. This result is in a similar manner of the propellant without iron oxide[1].

The ϕ_{min} of CAP and FAP is 55 wt% AP and 63 wt% AP, respectively[1]. The lower limit of AP content to combust can be decreased by the addition of iron oxide. The difference between $c\phi_{min}$ and ϕ_{min}, 33 wt%, of the propellant prepared with FAP is larger than that, 4 wt%, of the propellant prepared with CAP. This suggests that the effect of iron oxide on the decrease in the lower limit of AP content to combust becomes greater as the size of AP particle decreases.

In the case of the comparison of the heat generated at the burning surface of the propellant contained at $c\phi_{min}$, the heat quantity of the propellant prepared with CAP is larger than that of the propellant prepared with FAP because $c\phi_{min}$ of CAP is larger than that of FAP. At $c\phi_{min}$, the burning rates at 2 MPa of propellant prepared with FAP and CAP are 0.35 $\mathrm{mm \cdot s^{-1}}$ and 0.70 $\mathrm{mm \cdot s^{-1}}$, respectively. The heat generated on the burning surface and the burning rate of the propellant prepared with CAP are higher than these values of the propellant prepared with FAP, however the propellant prepared with CAP self-quenched nevertheless. These facts suggest that $c\phi_{min}$ was scarcely dependent on the heat quantity generated at the burning surface and the burning rate. It could be considered that the main cause of the self-quenched combustion was the mechanical condition on the burning surface and $c\phi_{min}$ was greatly dependent on the particle size and the distances between two adjacent AP particles in the similar result of the propellant without iron oxide[1]. It is necessary to investigate $c\phi_{min}$ and ϕ_{min} of AP which vary in size in order to examine the cause of the self-quenched combustion and clarify the relationship between $c\phi_{min}$ and ϕ_{min}.

The relationship between the burning rate and the AP content is shown in Fig.3. The burning rate decreases as the AP content decreases. For the propellant prepared with CAP, the decrement of the burning rate is slightly large between 80 wt% AP and 85 wt% AP, i.e., in the vicinity of the upper limit of AP content in propellant. Less than 80 wt% AP the burning rate decreases almost linearly with decreasing AP content. For the propellant prepared with FAP, the burning rate decreases greatly in the vicinity of the upper limit of AP content in propellant. The decrease of the burning rate becomes larger with increasing the pressure above 45 wt% AP and below that the decrease of the burning rate is independent on pressure.

3. 3 Effect of iron oxide on increase of burning rate

Iron oxide is the positive catalyst for the burning rate of AP/HTPB propellant. That is to say, the burning rate can be modified by the addition of iron oxide to the propellant. The inferences of the AP content, the particle diameter of AP and the pressure on the increment of the burning rate by the addition of iron oxide were discussed in this section.

The relationship between the burning rate and the AP content of the propellant without iron oxide is shown in Fig.3. The burning rate of the propellant without iron oxide is the data of Ref.1. The burning rates of the propellants added with iron oxide are larger than those of the propellants without iron oxide at all pressures. The decrease of the burning rate against AP content of the propellant added with iron oxide is smaller than that of the propellant without iron oxide in the vicinity of the upper limit of AP content. Especially, this tendency is more obviously in the case of the propellant prepared with FAP.

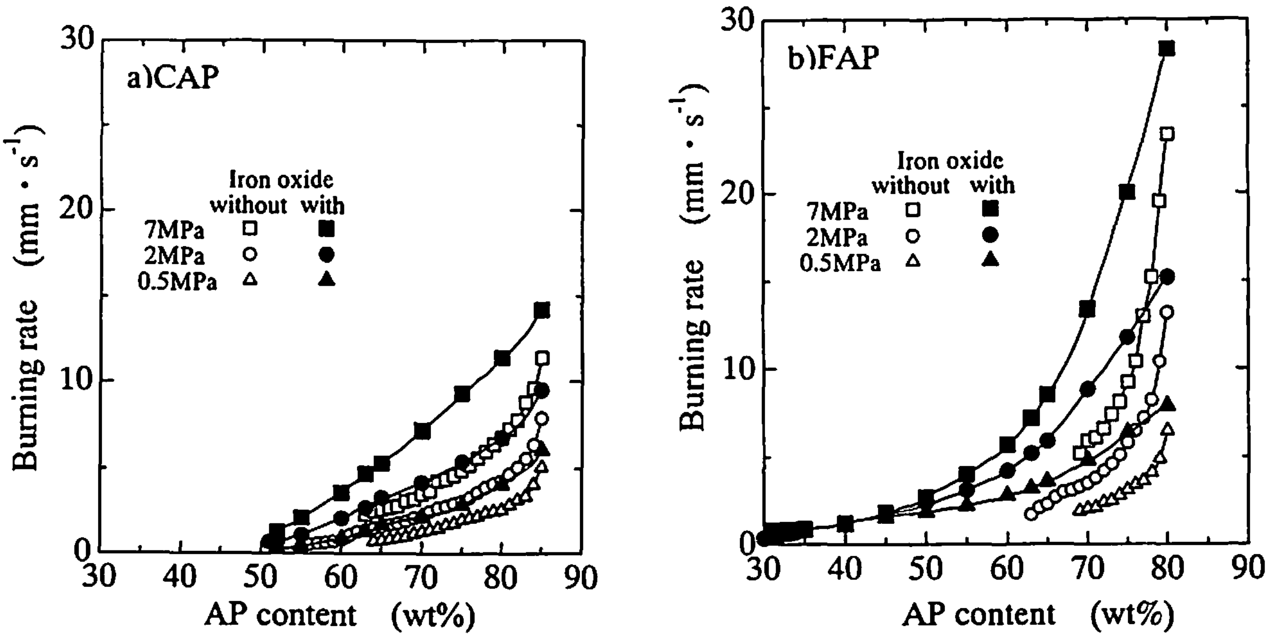

Fig.3 Relationship between burning rate and AP content

In order to make clear the effect of the addition of iron oxide on the increment of the burning rate, the ratio, *R* (-) of the burning rate of the propellant added with iron oxide to that of the propellant without iron oxide was calculated. The influence of the AP content on *R* is shown in Fig.4. The *R* is scarcely dependent on the pressure at the constant AP content. The *R* decreases with increasing AP content. This indicates that the effect of iron oxide on the increment of the burning rate decreases as the AP content increases. The decrease of *R* against AP content for the propellant prepared with FAP is lager than that for the propellant prepared with CAP. It is found that the effect of iron oxide on the increase of the burning rate is dependent on the AP content and the size of AP particle.

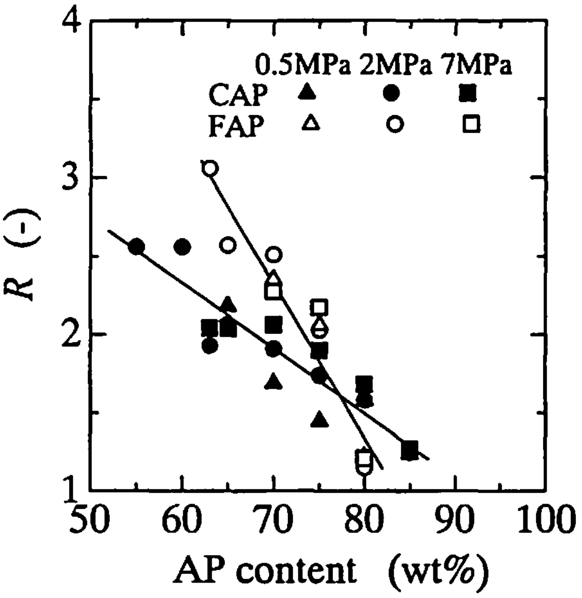

Fig.4 Influence of AP content on *R*

4. Conclusions

It is necessary to investigate the burning characteristics of furl-rich AP/HTPB composite propellant in order to develop a solid fuel of hybrid rocket. Iron oxide is used as a positive catalyst for the AP/HTPB composite propellant. The burning characteristics of fuel-rich AP/HTPB composite propellant added with iron oxide were investigated in this study. From this study the following conclusions were obtained : 1) The burning rate decreases as the AP content decreases, and the propellants self-quench less than a certain AP content. The self-quenched combustion occurs at a lower pressure and a higher pressure. 2) The possibility of combustion for fuel-rich AP/HTPB composite propellant added with iron oxide is dependent on the AP content, the particle size of AP, and the pressure. 3) The lower limit of AP content to combust is decreased by the addition of iron oxide. 4) The effect of iron oxide on the decrease in the lower limit of AP content to combust becomes greater as the size of AP particle decreases. 5) The effect of iron oxide on the increase of the burning rate is dependent on the AP content and the size of AP particle.

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酸化鉄を添加したFuel-rich AP/HTPB系コンポジット推進薬の燃焼特性

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ハイブリッドロケット用固体推進薬としてfuel-rich AP/HTPB系コンポジット推進薬の燃焼特性に関する研究が必要とされている。酸化鉄はAP/HTPB系コンポジット推進薬の燃焼触媒として用いられている。本実験では，酸化鉄を添加したfuel-rich AP/HTPB系コンポジット推進薬の燃焼特性について調べた。その結果，以下のことが明らかになった。1)AP含有率の減少にしたがい燃焼速度は減少し，あるAP含有率以下で中断燃焼が起こった。中断燃焼は低圧または高圧領域から起こった。2)酸化鉄を添加されたfuel-rich AP/HTPBコンポジット推進薬の燃焼が可能な範囲は，AP含有率，圧力範囲とAPの粒子径に依存することがわかった。3)酸化鉄を推進薬に添加することによって，燃焼可能なAP含有率の下限を減少できた。4)用いたAPの粒子径が小さいほど，酸化鉄添加による燃焼可能なAP含有率の下限の減少量は大きかった。5)酸化鉄による燃焼速度増加効果は，AP含有率と用いたAPの粒子径に依存した。

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