Article

Self-quenched combustion of fuel-rich AP/HTPB composite propellant

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In order to develop a solid propellant for gas hybrid rocket motor, it is required to investigate the burning characteristics of fuel-rich ammonium perchlorate (AP) based composite propellant. For fuel-rich composite propellant prepared with coarse AP and fine AP, the burning characteristics and the self-quenched combustion were investigated in this study. The following results were obtained: 1) The burning rate decreases as the AP content decreases, and the propellants contained less than a certain AP content self-quench. The self-quenched combustion occurs at a lower pressure and a higher pressure. 2) The lower limit of AP content to combust, φ_{min} exists. The φ_{min} of coarse AP is lower than that of fine AP. 3) It was found that the possibility of combustion for AP/HTPB composite propellant was dependent on the AP content, the particle size of AP, and the pressure. 4) The combustion of the propellant was self-quenched when AP particle did not expose on the burning surface. 5) The φ_{min} was directly independent on the heat generated on the burning surface and the burning rate. It could be considered that φ_{min} was greatly dependent on the particle size and the distances between two adjacent AP particles.

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 that a solid fuel can self-combust[1]. Gas hybrid rocket motor is explained as follows: A high temperature fuel-rich gas is generated by the combustion of a solid fuel in the gas generator. Thereafter, the high temperature fuel-rich gas is mixed with a gaseous or a liquid oxidizer and a high temperature gas is generated by the combustion of the mixed gas. This high temperature exhaust gas through a nozzle produces thrust.

Ammonium perchlorate (AP)/Hydroxyl terminated polybutadiene (HTPB) composite propellant is used most widely. Therefore, AP/HTPB composite propellant was used in this study. AP/HTPB composite propellant for gas hybrid rocket motor is a fuel-rich solid propellant. The burning characteristics of AP/HTPB composite propellant have been investigating until now. However, the burning characteristics of fuel-rich AP/HTPB composite propellant are not revealed sufficiently at present. It is necessary to investigate the burning characteristics of fuel-rich AP/HTPB composite propellant in order to use AP/HTPB composite propellant as a solid fuel for hybrid rocket motor.

As the AP content of AP/HTPB composite propellant decreases, the burning rate decreases, and the propellant self-quenches less than a certain AP content. Consequently, the lower limit of AP content to self-combust, φ_{min} (wt%) exists. A self-quenched propellant cannot be used as a solid fuel for hybrid rocket motor. It is generally known that the burning rate of AP/HTPB composite propellant increases with decreasing the mean diameter of AP particles. It was considered that the burning rate of fuel-rich AP/HTPB composite is dependent not only on the AP content but also on the particle diameter of AP. In this study, the fuel-rich AP/HTPB composite propellants were prepared with coarse AP and fine AP, and their burning characteristics and the self-quenched combustion were investigated. Some interesting results were obtained. Detail on the experiments is reported in this paper.

2. Experiment

Coarse AP (CAP) and fine AP (FAP) were used as oxidizer in this study. 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 scanning electron microscope (SEM) photographs of these AP samples are shown in Fig.1.

Received: November 21, 2002
Accepted: January 7, 2003
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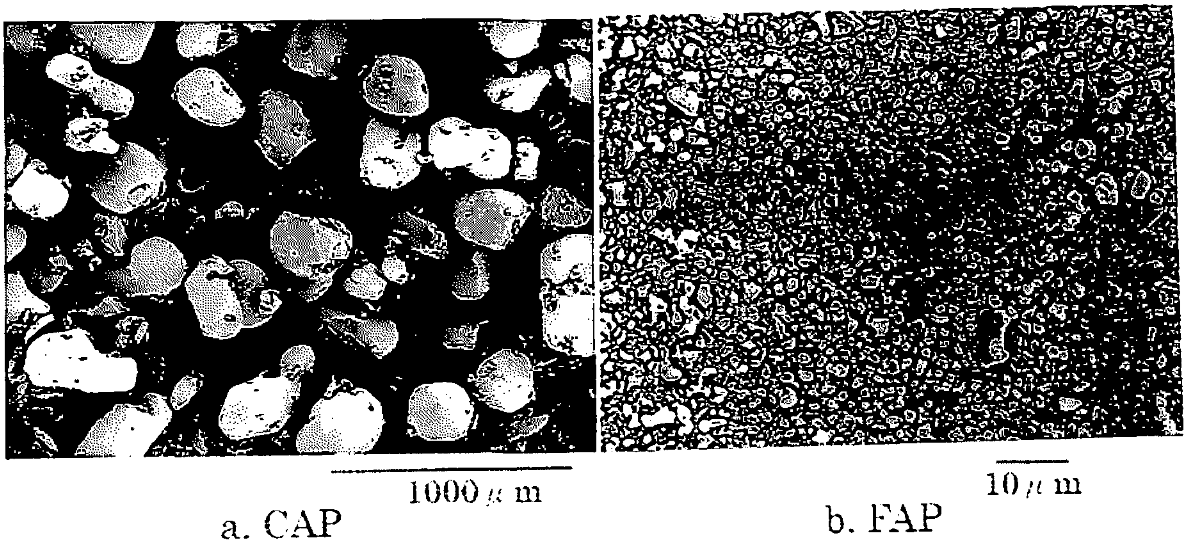


Fig.1 SEM photographs of CAP and FAP

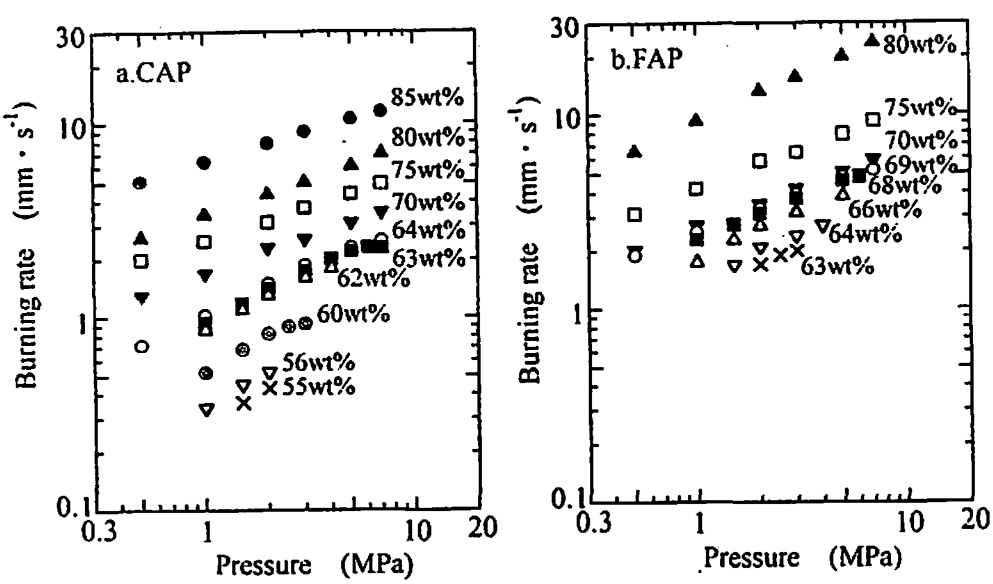


Fig.2 Burning rate characteristics

The shape of AP used in this study was almost spherical and the mean particle diameters of CAP and FAP were about 110 μm and 4 μm, respectively. 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 then cured for 4 days at 333 K.

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 burning of propellant sample was conducted with the 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. It is judged that the propellant cannot combust when one in the three lots of propellants self-quenched.

3. Results and discussion

3.1 Burning rate characteristics

Because of the requirements for the preparation of AP/HTPB composite propellant, the upper limit of AP content in propellant exists[3)4)]. The upper limits of AP content in propellants prepared with FAP and CAP are 80 wt% AP and 85 wt% AP, respectively[3)4)]. About each AP sample, the propellant samples were prepared less than the upper limit of AP content in propellant. The burning rates of the propellants were measured. 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 64 wt% AP combust in the pressure range adopted in this study. The propellant contained at 63 wt%AP self-quenches at 0.5 MPa, and the propellant contained at 62 wt% AP self-quenches also between 5 MPa and 7 MPa. The combustible pressure range decreases with decreasing AP content. The propellant contained at 55 wt% AP combusts only between 1.5 MPa and 2 MPa, and the propellant contained at 54 wt% AP does not combust in the pressure range adopted in this study.

In regard to the propellant prepared with FAP, the propellants contained above 69wt% AP combust between 0.5 MPa and 7 MPa. The propellant contained at 68 wt%AP self-quenches at 0.5 MPa and 7 MPa. The combustible pressure range decreases with decreasing AP content. The propellant contained at 63 wt% AP combusts only between 2 MPa and 3 MPa, and the propellant contained at 62 wt% AP does not combust in the pressure range adopted in this study. These results indicate that φ_{min} of CAP and FAP is 55 wt% AP and 63 wt% AP, respectively. The φ_{min} of coarse AP is lower than that of fine AP. These results suggest that the possibility of combustion for AP/HTPB composite propellant is dependent on the AP content, the particle size of AP and the pressure.

In order to make more clear the effect of the AP content on the burning rate, the relationship between the burning rate and the AP content is illustrated graphically in Fig.3. The burning rate decreases as the AP content decreases. The burning rate decreases greatly in the vicinity of the upper limit of AP content in propellant. The decrease in the burning rate of the propellant prepared with FAP is larger than that of the propellant prepared with CAP. For the propellant prepared with FAP, the reduction of the burning rate increases as the pressure increases and that for the propellant prepared with CAP is scarcely dependent on the pressure.

As mentioned above, φ_{min} of CAP and FAP is 55 wt% AP and 63 wt% AP, respectively. In regard to the propellant contained at φ_{min}, the heat generated on the burning surface of the propellant prepared with FAP is larger than that of the propellant prepared with CAP because ϕ_{min} of FAP is larger than that of CAP. At 63 wt% AP, which is ϕ_{min} of FAP, the burning rates at 2 MPa of propellant prepared with FAP and CAP are 1.7 $mm \cdot s^{-1}$ and 1.4 $mm \cdot s^{-1}$, respectively. The heat generated on the burning surface and the burning rate of the propellant prepared with FAP are higher than these values of the propellant prepared with CAP, however the propellant prepared with FAP self-quenches nevertheless. This result suggests that φ_{min} was directly dependent on the heat generated on 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 as discussed in the next section.

3.2 Process of self-quenched combustion

3.2.1 Observation of self-quenched burning surface

The self-quenched burning surface was observed with SEM in order to examine the cause of the self-quenched

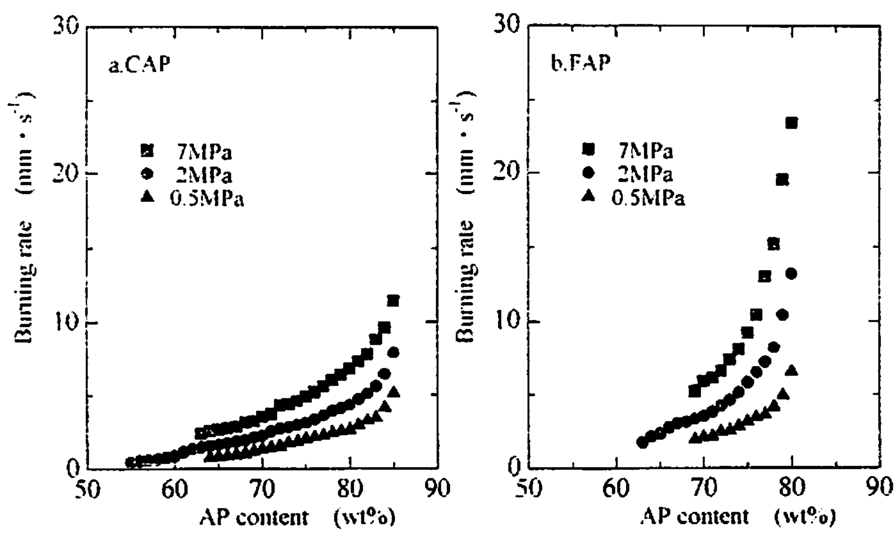
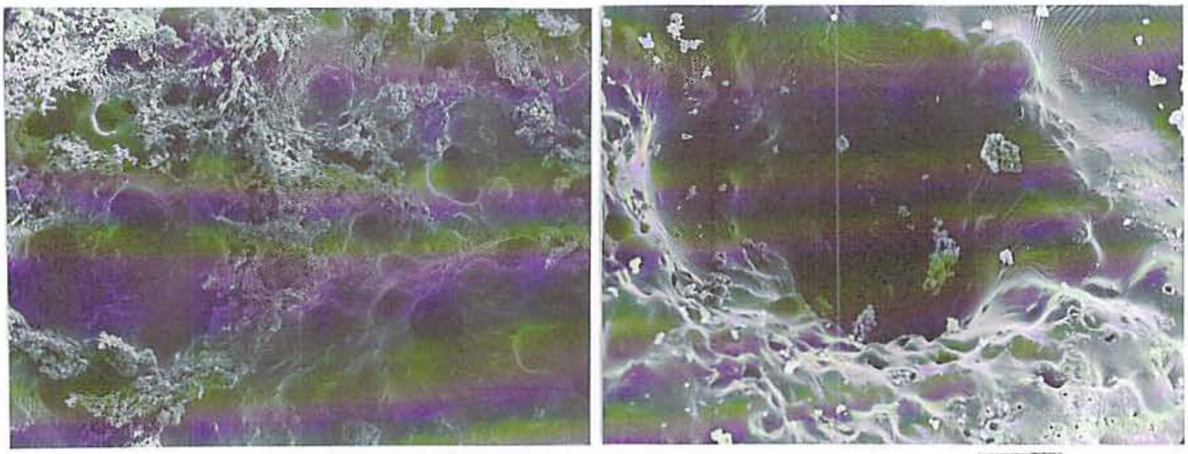


Fig.3 Relationship between burning rate and AP content

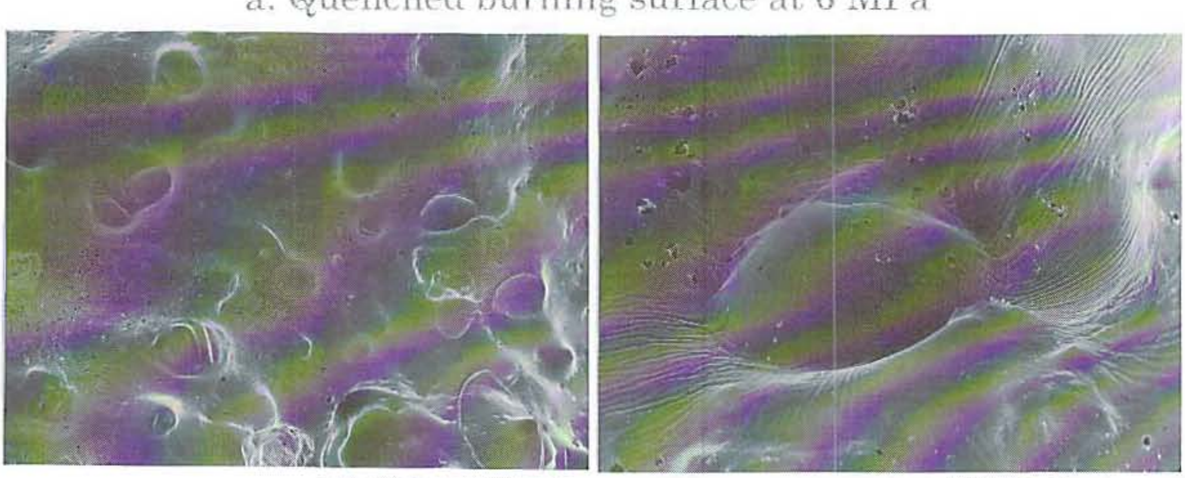
combustion. Fig.4 shows the SEM photographs of the burning surfaces self-quenched at 6 MPa and 1 MPa for the propellant prepared with CAP at 55 wt% AP. Figs.4 (a-2) and (b-2) are the photographs enlarged a part of Figs.4 (a-1) and (b-1), respectively. According to Fig.4 (a), some holes are observed on the burning surface self-quenched at 6 MPa. The size of hole is almost the same as the particle diameter of CAP. It can be considered that the hole was the trace of AP particle. The AP particle does not remain in all holes. According to Fig.4 (b), the hole such as that at 6 MPa is not observed on the burning surface self-quenched at 1 MPa and some striped patterns of HTPB are observed on the self-quenched burning surface. HTPB melts before the decomposition. It can be considered that the stripes were the trace of the flow of melted HTPB. The AP particle is not observed on the self-quenched burning surface. The convex surface is observed in Fig.4 (b-2). The size of the convex is almost the same as that of AP particle. It can be supposed that there was the AP particle just under the HTPB layer on the convex surface. It could be presumed that the melted HTPB was covered on the burning surface of AP particle.

Fig.5 shows the SEM photographs of the burning surfaces self-quenched at 4 MPa and 1 MPa for the propellant prepared with FAP at 63 wt% AP. According to Fig.5 (a), some holes is observed on the burning surface self-quenched at 4 MPa. The size of hole is almost the same as the particle diameter of FAP. The AP particle does not remain in all holes. According to Fig.5 (b), the burning surface self-quenched at 1 MPa is almost flat and any hole is not observed on the burning surface. It is found that AP particles do not expose on these self-quenched burning surfaces through the observation of the self-quenched burning surface.



(a-1) 1000 μm (a-2) 100 μm

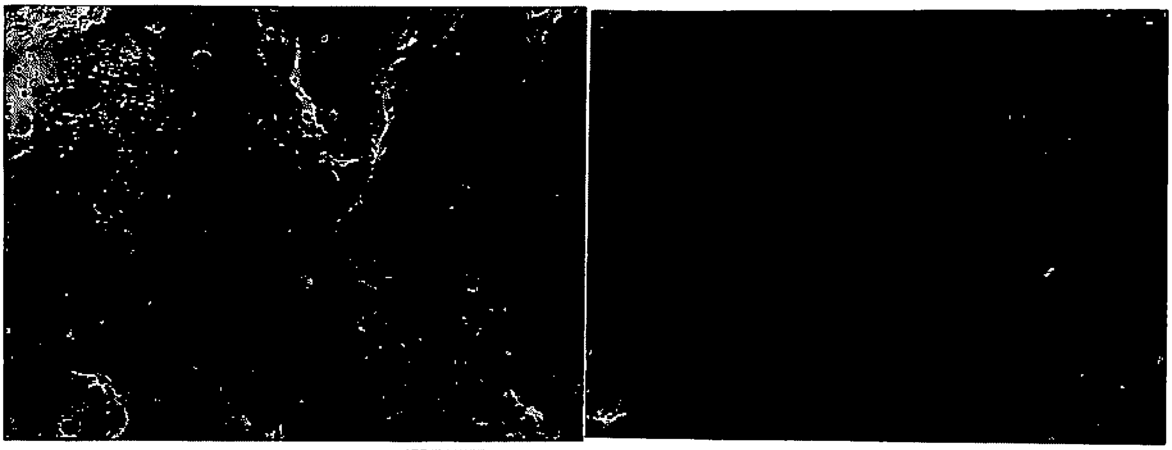
a. Quenched burning surface at 6 MPa



(b-1) 1000 μm (b-2) 100 μm

b. Quenched burning surface at 1 MPa

Fig.4 SEM photographs of quenched burning surface of propellant prepared with CAP



10 μm
a. Quenched burning surface at 4 MPa

10 μm
b. Quenched burning surface at 1 MPa

Fig.5 SEM photographs of quenched burning surface of propellant prepared with FAP

3. 2. 2 Qualitative analysis

When the burning surface of a propellant extinguished by rapid depressurization was observed, at a lower pressure the AP particles protrude above the exposed surface of the binder to a greater height and at a higher pressure they recess[5,6]. This fact indicates that at a low pressure the regression rate of the AP burning surface is less than that of the HTPB burning surface and vice versa at higher pressures.

The flame of AP composite propellant is a so called diffusion flame, and the model of Multiple Flames[7] is generally accepted as a model of the flame structure. According to the model of Multiple Flames, the flame structure of AP composite propellant consists of the AP monopropellant flame, the primary flame, and the final diffusion flame. The AP particle on the burning surface sublimes and does not melt. The AP decomposition products compose the AP monopropellant flame. HTPB melts and thereafter decomposes. The primary flame and the final diffusion flame are composed by the combustion of these decomposition products. AP and HTPB can be decomposed by the heat generated at the burning surface and in the flames. By means of the continuance of this routine, the combustion of the propellant can be sustained and the burning surface regresses.

AP can decompose and combust continuously because the decomposition of AP is exothermically and AP decomposition products compose the AP monopropellant flame. On the other hand, HTPB cannot decompose on the burning surface independently because HTPB is allowed to decompose by means of the enough heat generated at the burning surface and in the flames. It is necessary that AP is first decomposed and the AP monopropellant flame is formed with the AP decomposition products in order to combust the AP/HTPB composite propellant. This suggests that the combustion of the propellant is self-quenched when AP particle does not expose on the burning surface. The HTPB layer between two adjacent AP particles should be decomposed before the AP particles on the burning surface was disappeared by the decomposition in order to maintain the combustion of the propellant. As the AP content decreases, the HTPB layer between two adjacent AP particles becomes thicker and, that is, the self-quenched combustion was easier.

The cause of the self-quenched combustion was presumed as follows on the basis of the above considerations. The self-quenched combustion occurs at a lower pressure and a higher pressure. First, the reason of the self-quenched combustion in a higher pressure was discussed. Fig.6 shows the schematic diagram of the burning surface structure. The regression rate of the AP burning surface is faster than that of the HTPB burning surface at higher pressures[5,6]. The AP burning surface is lower than the HTPB burning surface (Figs.6 (a-2) and (a-3)). Before the AP particles on the burning surface was disappeared by the decomposition, the HTPB layer between two adjacent AP particles could not decompose (Fig.6 (a-4)). Consequently, the flame could not propagate to the next plane of AP particle and the combustion of the propellant was self-quenched at higher pressure.

Second, the reason of the self-quenched combustion in a lower pressure was discussed. At a low pressure the regression rate of the AP burning surface is less than that of

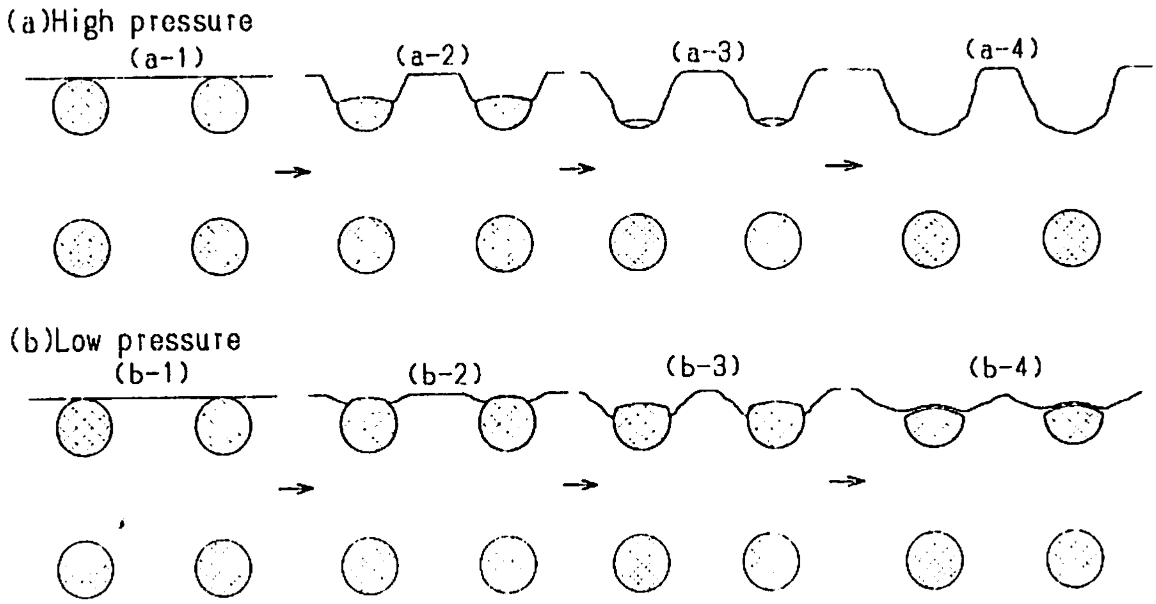


Fig.6 SEM photographs of quenched burning surface of propellant prepared with FAP

the HTPB burning surface[5)6)]. The HTPB burning surface could regress faster than the AP burning surface in the vicinity of the AP particle and, however, the entire burning surface of HTPB between two adjacent AP particles could not regress faster than that of the AP particle (Fig.6 (b-2)). This is because the distance between two adjacent AP particles increases, and the net heat of reaction at the burning surface decreases and the heat feedback from the flames to the burning surface decreases as the AP content decreases. When the decomposition of AP and HTPB proceeded to some extent at the burning surface, a depression was formed (Fig.6 (b-3)). The HTPB is melted and, thereafter, decomposed by the heat generated at the burning surface and in the flames. The melted HTPB in the vicinity of AP particle would flow into the depression and cover the burning surface of AP before the melted HTPB was disappeared by the decomposition (Fig.6 (b-4)). Therefore, AP particle could not expose on the burning surface and the combustion of the propellant self-quenched.

The distance between two adjacent AP particles for the propellant contained at φ_{min} was calculated theoretically on the hypothesis that AP particle was spherical and the size was constant. The distances for the propellant prepared with FAP and CAP are 0.2 μm and 14.5 μm, respectively. The distance for the propellant prepared with FAP is smaller than that for the propellant prepared with CAP.

As mentioned above, it could be considered that the main cause of the self-quenched combustion was the mechanical condition on the burning surface, and φ_{min} was greatly dependent on the particle size and the distances between two adjacent AP particles. The value of φ_{min} could not be revealed quantitatively in this study. It is necessary to investigate φ_{min} of AP which vary in size in order to clarify the relationship among φ_{min}, the particle size and the distances between two adjacent AP particles.

4. Conclusions.

Gas hybrid rocket motor has been developing for a hybrid 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 propellant for gas hybrid rocket motor. In regard to fuel-rich AP/HTPB composite propellant prepared with coarse AP and fine AP, the burning characteristics and the self-quenched combustion were investigated in this study. From this study the following conclusions were obtained: 1) As the AP content decreases, the burning rate decreases and the propellants self-quench at less than a certain AP content. The self-quenched combustion occurs at a lower pressure and a higher pressure. 2) The lower limit of AP content to combust, φ_{min} exists. The φ_{min} of coarse AP is lower than that of fine AP. 3) It was found that the possibility of combustion for AP/HTPB composite propellant was dependent on the AP content, the particle size of AP and the pressure. 4) The combustion of the propellant is self-quenched when AP particle does not expose on the burning surface. 5) The φ_{min} was directly dependent on the heat generated on the burning surface and the burning rate. It could be considered that φ_{min} was greatly dependent on the particle size and the distances between two adjacent AP particles.

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Fuel-rich AP/HTPB系コンポジット推進薬の中断燃焼

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ハイブリッドロケット用固体推進薬の開発のために，Fuel-rich AP/HTPB系コンポジット推進薬の燃焼特性を明らかにする必要がある。本実験では，粗粒または微粒APを用いて製造されたFuel-rich AP/HTPB系コンポジット推進薬の燃焼速度特性及び中断燃焼について調べた。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)燃焼可能なAP含有率の下限，ϕ_{min}が存在した。粗粒APを用いた推進薬のϕ_{min}は，微粒APを用いた推進薬のそれより小さかった。3) AP/HTPB系コンポジット推進薬の燃焼が可能な範囲は，AP含有率，APの粒子径及び圧力に依存することがわかった。4)燃焼表面にAP粒子が露出しない場合，推進薬の燃焼は中断することがわかった。5) ϕ_{min}は燃焼速度と燃焼表面上で発生する熱量には直接的に影響されず，APの粒子径とAP粒子間の距離に大きく依存する。

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