Article

# AP/HTPB composite propellant using fine hollow AP prepared by spray-drying method

Makoto Kohga*, and Yutaka Hagihara*

Fine ammonium perchlorate (AP) is required in order to prepare a high burning rate AP based composite propellant. Fine hollow AP (FAP), of which the mean volume-surface diameter is about 2.7μm, is prepared by the spray-drying method. The crystallographical property and the thermochemical behavior of FAP, and the productivity and the burning rate characteristics of the propellant prepared with FAP were investigated in this study. The results were as follows; The crystallographical property and the thermochemical behavior of FAP are almost the same as those of the ground commercial AP (CAP). The upper limit of the FAP content in propellant is 72 wt%. The propellant was prepared at 80 wt% AP with a bimodal AP, FAP and CAP. The burning rate of the propellant contained 80 wt% AP with a bimodal AP, which was different in the relative amounts of FAP and CAP, increases with increasing the content of FAP. The increment of burning rate at high pressures is larger than that at low pressures. It is found that FAP is an effective oxidizer for the increase in the burning rate.

## 1. Introduction

The high burning rate propellant has been required. Recently ammonium perchlorate (AP) / hydroxyl terminated polybutadiene (HTPB) composite propellant is used widely. It is generally known that the burning rate of AP/HTPB composite propellant increases with decreasing the particle diameter of AP contained in propellant. In order to obtain the high burning rate AP/HTPB composite propellant, fine AP is required. However, it is difficult to prepare fine AP particles safely by grinding[1)2)] because fine AP is ignited and exploded easily by slight impact or friction. Some safe methods of preparing fine AP particles have been developing until now[3)-6)]. It is reported that fine AP can be prepared safely by a spray-drying method described below[7)]. Fine droplets of AP solution are sprayed by ultrasonic atomizer. The fine droplets are dried by a spray-dryer. Inlet temperature and flow rate of surround air are 313 K and 0.010 $m^3 \cdot s^{-1}$, respectively. The fine AP prepared by this spray-drying method was designated as FAP. FAP is a hollow particle and the mean volume surface diameter is approximately 2.7μm[7)].

On the other hand, the burning rate can be increased by the fine bubbles, which is distributed independently one another, in the propellant[9)]. There is a void in FAP particle because FAP is a hollow particle. The size of void in FAP is smaller than the particle size. Therefore, the void is very small. It can be considered that there was numerous fine bubbles distributed independently one another in a propellant containing FAP since binder could not flow into the void in FAP. Consequently, it can be expected that the high burning rate AP/HTPB composite propellant could be prepared by the use of FAP as an oxidizer. In the present study, it is reported that the crystallographical property and the thermochemical behavior of FAP, and the burning rate characteristics of the propellant containing FAP.

## 2. Experimental

In this study, two kinds of AP were used as an oxidizer: one was FAP and another was a ground commercial AP (CAP). The CAP was prepared by grinding a commercial AP for 5 minutes with a vibration ball mill. The mean volume surface diameter of CAP is 110μm. The CAP was used in order to compare with the crystallographical property and the thermochemical behavior of FAP, and the burning rate characteristics of the propellant containing FAP.

The crystallographical property of AP was examined by X-ray diffractometry (XRD). The XRD was carried out using a Rigaku GEIGERFLEX RAD-ⅢA. The characteristic X-ray wavelength is CuK$\alpha$ ($\lambda$=1.5418Å).

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*Department of Applied Chemistry, National Defense Academy, 1-10-20, Hashirimizu, Yokosuka-shi, Kanagawa, 239-8989, JAPAN
TEL +81-468-41-3810 (ext. 3585)
FAX +81-468-44-5901
E-Mail kohga@nda.ac.jp

Thermochemical behavior of AP was investigated by differential thermal analysis (DTA) and thermogravimetry (TG). DTA and TG were carried out using a Rigaku TAS-100 Thermal Analyzer. The equipment was operated in a nitrogen flow condition at atmospheric pressure. The sample containers for the equipment were made of aluminum. The sample weight was about 5 mg. The heating rate was 20 K/min. The drop hammer test for AP was conducted on the basis of Japanese Explosive Standard ES-21 (1) [10].

In this study the propellants were prepared at 80 wt% AP. The HTPB was used as a binder. The HTPB was cured with isophorone diisocyanate (IPDI) of a crosslinking agent. IPDI was added to 8 wt% of HTPB. The density of a propellant was measured by a suspend method[11]. The size of each propellant 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 at 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 rate was measured in pressure range of 0.5 MPa – 7 MPa, and was calculated with the cutoff period of two fuses which penetrate the strand at 25 mm distance.

## 3. Results and discussion

### 3. 1 XRD pattern of AP

The FAP is recrystallized in very short time since FAP is prepared by the spry-drying method. It was possible that FAP would have crystal defect. The crystallographical properties of FAP and CAP were examined by XRD. When the maximum intensity was identified as 100 on the basis of the measured XRD pattern of FAP or CAP, the XRD pattern was reillustrated. The XRD patterns of CAP and FAP are shown in Fig.1. The XRD pattern of FAP is almost the same as that of CAP. Consequently, it is found that crystal habits of FAP is not modified.

The crystal defect in AP used was investigated by the Hall's method[12]. The magnitude of the crystal defect, σ, is represented by the following equation.

$$\frac{\beta\cdot\cos\theta}{\lambda} = \frac{1}{\eta} + \frac{2\sigma}{E_{hkl}}\cdot\frac{\sin\theta}{\lambda} \qquad (1)$$

$\beta$ is the half width, $\theta$ is the Bragg angle of diffraction, $\lambda$ is the X-ray wavelength and $\eta$ is the effective particle size. The $E_{hkl}$ is the value of Young's modulus for the direction perpendicular to the planes{hkl}. The $\beta$ can be measured from the XRD pattern. When $E_{hkl}$ is assumed to be constant[12)-14)], a plot of $\beta\cdot\cos\theta/\lambda$ against $\sin\theta/\lambda$ is linear. From the slope of the straight line, $2\sigma/E_{hkl}$, that is, $\sigma$ can be calculated[12)-14)]. The relationship between $\beta\cdot\cos\theta/\lambda$ and $\sin\theta/\lambda$ is shown in Fig.2. Both slopes of the straight lines of FAP and CAP are approximately zero.

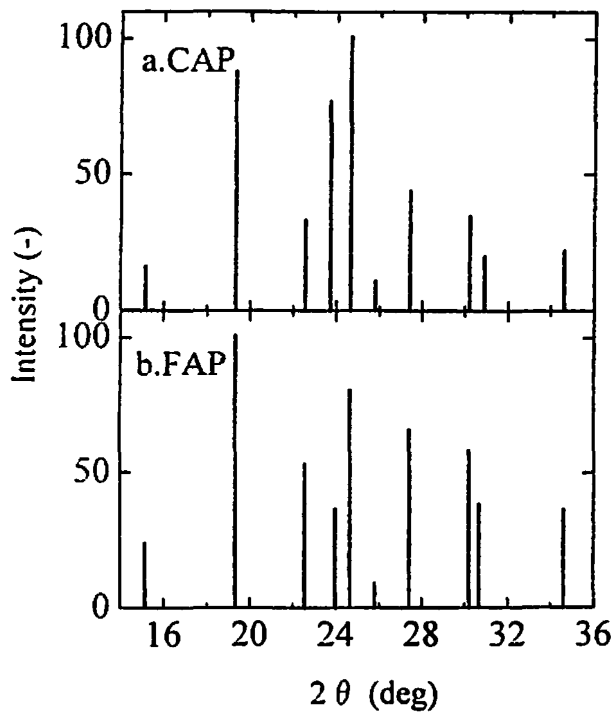


Fig.1 X-ray diffraction patterns

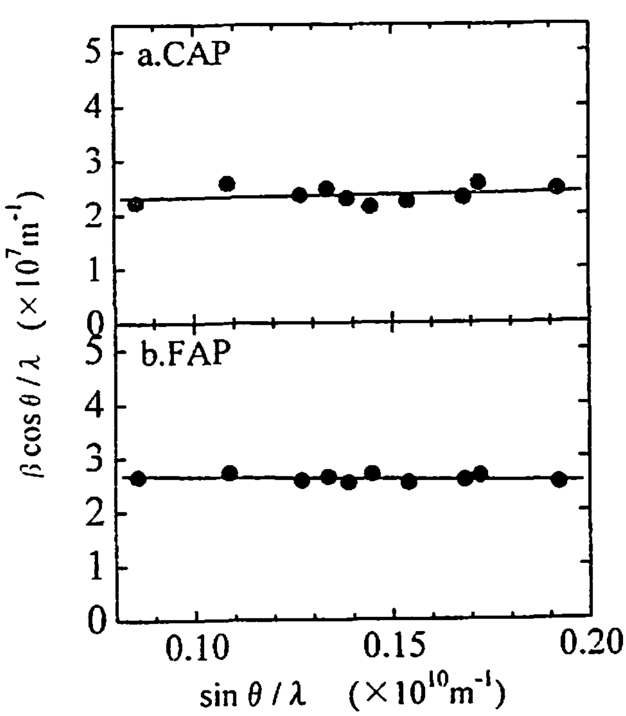


Fig.2 Relationship between βcosθ/λ and sinθ/λ

This indicates that FAP and CAP do not develop the crystal defect, even if FAP is recrystallized rapidly by a spray-drying method and CAP is ground with the vibration ball mill. It is found that the crystallographical properties of FAP were almost the same as those of CAP in this study.

### 3. 2 Thermochemical behavior of AP

For the typical DTA thermogram[15], the endothermic peak of crystal transformation of AP from orthorhombic to cubic structure is observed at 516 K. Subsequently there are two exothermic decompositions, namely, a low temperature decomposition and a high temperature decom position. For the typical TG thermogram[15], a slight consumption of AP starts at the beginning temperature of a low temperature decomposition. A consumption of AP at a low temperature decomposition is a little and does not affect consumption of AP at a high temperature decomposition. At a high temperature decomposition, a rapid consumption of AP occurs and AP is consumed completely. The DTA and TG thermograms of FAP and CAP are shown in Fig.3. The DTA and TG thermograms of FAP are almost the same as these thermograms of CAP, respectively. Fig.3 indicates that thermochemical behavior of FAP and CAP are almost the same as the typical behavior of AP.

Consumption of AP at a low temperature decomposition increases with increasing the proportion of a crystal defect in AP crystal[15]. As shown in Fig.3, consumption at the low temperature decomposition of FAP and CAP is a little. This fact indicates that a crystal defect of FAP and CAP is little. This result supports the result obtained from XRD pattern.

### 3. 3 Drop hammer test

The sensitivity of AP on impact increases with decreasing particle size. It is predicted that the sensitivity of FAP is high, because FAP is a fine particle. If the sensitivity of FAP was very high, FAP could not be used as an oxidizer of a composite propellant. According to the results of the drop hammer test, the sensitivity classes of FAP and CAP are 4 and 7, respectively. The sensitivity class of FAP is higher than that of CAP. However, the sensitivity class of FAP is almost the same as that of RDX and HMX. FAP can be used as an oxidizer of a composite propellant with taking sufficient care not to impact it.

### 3. 4 Thermochemical behavior of AP

As described in section 2, the propellant was prepared at 80 wt% AP in this study. It is required for the preparation of

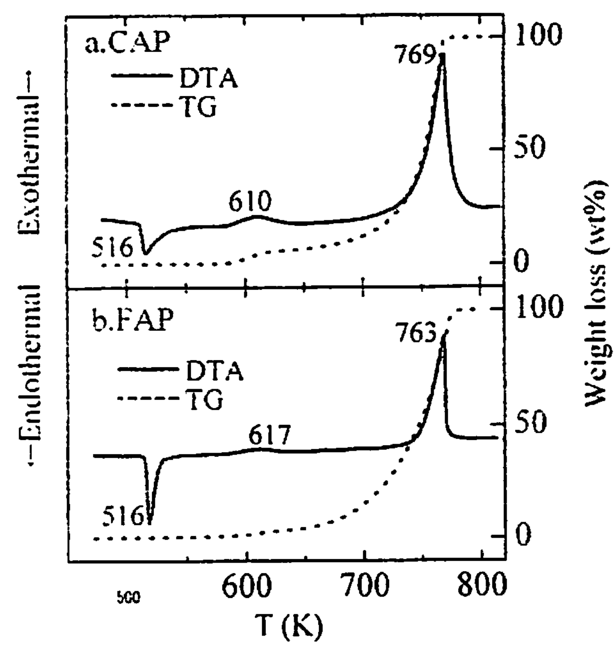


Fig.3 DTA and TG thermograms

AP/HTPB composite propellant that uncured propellant has a viscosity required for casting and the proportion of bubble contamination in propellant is less than 2.0 vol%. Owing to these two requirements for the preparation of AP/HTPB composite propellant, the upper limit content of AP contained in propellant exists[16]. It could be presumed that the upper limit content of FAP was less than 80 wt% because the upper limit content of fine AP is small. According to Ref.16, the upper limit content of FAP was investigated. First, the uncured propellants are prepared at various AP contents and the largest AP content in the uncured propellants which have the viscosity required for casting is determined. Second, three lots of propellants were prepared at same AP content. The AP content was decreased by 1 wt% from the largest AP content in the uncured propellants which have the viscosity required for casting. When the proportion of bubble contamination in propellant is less than 2.0 vol%, the reproducible burning rate is obtained[16] and the relationship between burning rate and pressure follows Vieille's law according to the experience in this laboratory. As mentioned above, three lots of propellants are prepared at same AP content. When the burning rates of these propellants are reproducible and the relationship between the burning rate and pressure follows Vieille's law, it is judged that the burning rate of the propellant is not influenced by the bubble contamination, that is, the proportion of bubble contamination in propellant is less than 2.0 vol%. In this study, the upper limit of AP content was determined as the largest AP content in the propellants, of which the reproducibility of the burning rate can be obtained and of which relationship between burning rate and pressure follows Vieille's law.

Fig.4 shows the burning rate characteristics of the propellants prepared with only FAP. When the AP content is less than 72wt%, the reproducibility of the burning rate can be obtained and the burning rate increases lineally in a plot of ln (burning rate) versus ln (pressure), that is, the relationships follow Vieille's law. When the AP content is 73 wt%, the reproducibility of the burning rate cannot be obtained and the burning rate does not increase lineally in a plot of ln (burning rate) versus ln (pressure), that is, the relationship does not follow Vieille's law. These results indicate that the upper limit of AP content of the propellant prepared with only FAP is 72 wt%. It is found that the propellant contained at 80 wt% AP cannot be prepared with only FAP.

The upper limit of AP content of the propellant prepared with bimodal AP, mixing fine AP and coarse AP, is larger than that of the propellant prepared with only fine AP[17]. CAP was used as coarse AP and an attempt was made to prepare the propellant contained at 80wt% AP with bimodal AP mixing FAP and CAP. When the mass ratio of FAP to CAP is 1:1, the upper limit content of AP contained in propellant prepared with bimodal AP is 80 wt%. The propellants contained at 80 wt% AP were prepared with a bimodal AP which was different in the relative amounts of FAP and CAP, in order to investigate the effect of the FAP content in total AP (FAP/total AP) on the burning rate. Table1 shows the formulation of propellant prepared with bimodal AP. The burning rates of propellants A-D were measured. The

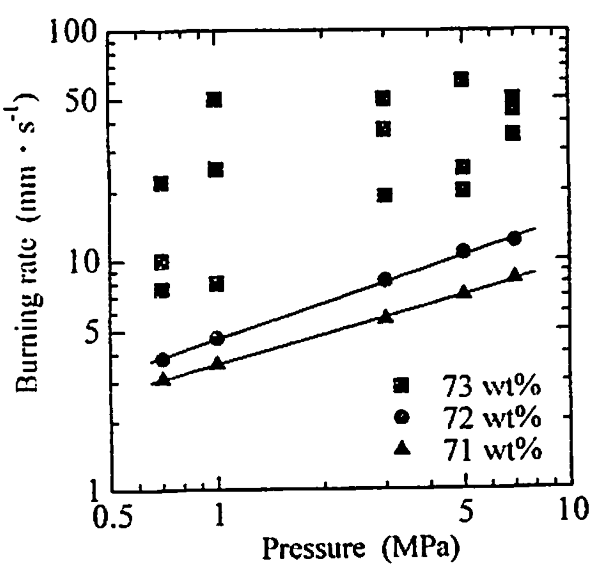


Fig.4 Burning rate characteristics of propellant prepared with only FAP

Table 1 Formulation of propellant prepared with bimodal AP

| Symbol | FAP (wt%) | CAP (wt%) | HTPB (wt%) |
|---|---|---|---|
| A | 0 | 80 | 20 |
| B | 8 | 72 | |
| C | 24 | 56 | |
| D | 40 | 40 | |

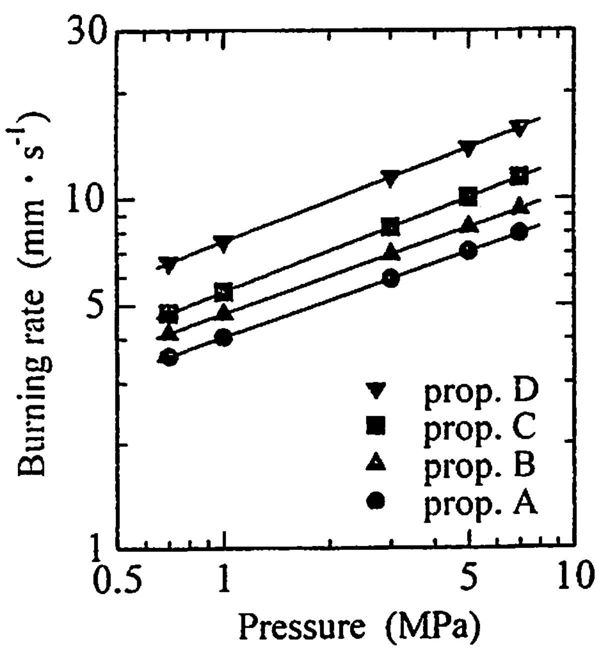


Fig.5 Burning rate characteristics of propellants A-D

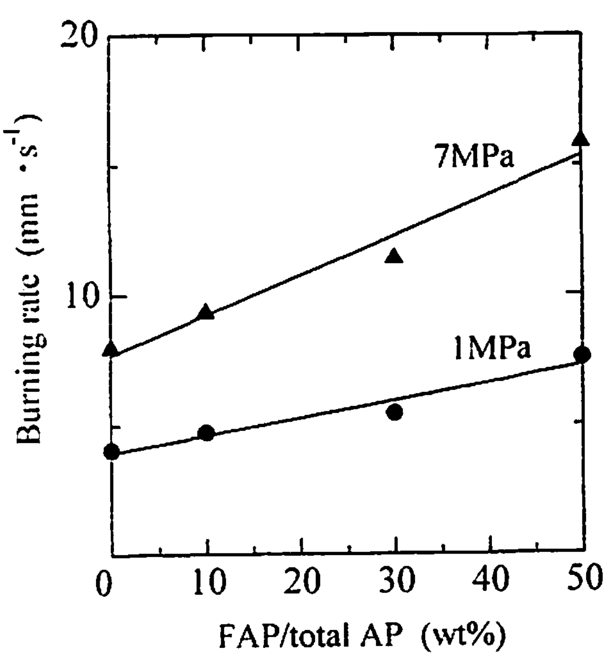


Fig.6 Effect of FAP content on burning rate

burning rate characteristics of those propellants are shown in Fig.5. Their burning rates increase linearly in a plot of ln r versus ln P in the pressure range of 0.5 – 7 MPa. The burning rate increases with increasing FAP/total AP.

In order to make clear the effect of the FAP content on the increment of the burning rate, the relationship between the burning rate and FAP/total AP is shown in Fig.6. The burning rate increases with increasing FAP/total AP and, especially, the increment of burning rate at 7 MPa is larger than that at 1 MPa. The burning rate at 7 MPa is approximately doubled by substituting half of CAP with FAP.

According to the results in this investigation, it is found that FAP is an effective oxidizer to prepare the high burning rate AP/HTPB composite propellant.

## 4. Conclusions

Fine hollow ammonium perchlorate (FAP) is prepared by the spray-drying method. The crystallographical property and the thermochemical behavior of FAP, and the productivity and the burning rate characteristics of the propellant prepared with FAP were investigated in this study. The results were as follows ; The crystallographical property and the thermochemical behavior of FAP are almost the same as those of the ground commercial AP (CAP). The upper limit of the FAP content in propellant is 72 w%. The propellant was prepared at 80 wt% AP with a bimodal AP, FAP and CAP. The burning rate of the propellant contained at 80 wt% AP with a bimodal AP, which was different in the relative amounts of FAP and CAP, increases with increasing the content of FAP. The increment of burning rate at high pressures is larger than that at low pressures.

It is found that FAP is an effective oxidizer for the increment of in the burning rate.

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# 噴霧乾燥法で調製された微粒な中空 AP を用いた AP/HTPB 系コンポジット推進薬

甲賀 誠*，萩原 豊*

高燃焼速度を有する AP 系コンポジット推進薬が要求されている。噴霧乾燥法によって，体面積平均径 2.7μmの微粒な中空過塩素酸アンモニウム(FAP)が調製された。本実験では，FAP の結晶学的性質と熱分解性について調べるとともに，FAP を用いた推進薬の燃焼速度について調べた。その結果，以下のことが明らかにされた。FAP の結晶学的性質と熱分解性は，粉砕された市販の AP(CAP)のそれとほぼ同じであった。FAP のみを用いて推進薬を製造した場合，推進薬に混入できる AP 含有率の上限は 72 wt%であった。FAP の一部を CAP に置き換えることによって，AP 含有率 80 wt%の推進薬を製造できた。AP 含有率 80 wt% において，FAP と CAP の混合割合を変化させて推進薬を製造したところ，それらの燃焼速度は FAP の混合割合が増加するにしたがい大きくなった。高圧部における燃焼速度の増加量は低圧部のそれより大きかった。以上の結果から，高燃焼速度の AP/HTPB 系コンポジット推進薬を製造するために，FAP は有効な酸化剤であることがわかった。

(*防衛大学校 応用化学科 〒239-8989 横須賀市走水 1－10－20)