

AP/HTPB composite propellant using fine AP prepared by freeze-drying method (IV)

— Fine AP prepared from emulsion with toluene and AP solution —

Makoto KOHGA* and Yutaka HAGIHARA*

Fine ammonium perchlorate (FAP), of which the mean volume-surface diameter is about 3.9 μm , is prepared by freeze-drying method. The crystallographical property and the thermochemical behavior of FAP, and the productivity and burning rate characteristics of the propellant prepared from FAP were investigated in this study. Hydroxyl-terminated polybutadiene (HTPB) was used as a binder. The results are as follows; 1) The crystallographical property and the thermochemical behavior of FAP are almost the same as those of the commercial AP. 2) The upper limit content of FAP containing propellant, ϕ_{max} (wt%), is 80wt%. The burning rate measured at 7MPa of the propellant containing 80wt%FAP is 24.6mm/s. 3) The burning rate increases with increasing the FAP content. The increment of the burning rates at high pressures is larger than that at low pressures, and particularly the increment of the burning rate increases greatly with coming close to ϕ_{max} . 4) When HTPB prepolymer added sodium lauryl sulfate was used as a binder, ϕ_{max} of the propellant prepared from FAP was 82wt%. By the use of HTPB prepolymer added sodium lauryl sulfate, ϕ_{max} of FAP could be increased by 2wt%. The burning rate measured at 7MPa of the propellant containing 82wt%FAP was 30.1mm/s. The burning rate could be increased by a slight increase in ϕ_{max} of FAP. It is found that FAP is an effective oxidizer to prepare high burning rate AP/HTPB composite propellant.

1. Introduction

Ammonium perchlorate (AP)/hydroxyl terminated polybutadiene (HTPB) composite propellant is the most widely used composite propellant. Recently a high burning rate composite propellant has been required. It is generally known that the burning rate of AP/HTPB composite propellant increases with decreasing the particle diameter of AP contained propellant. In order to obtain the high burning rate AP/HTPB composite propellant, fine AP is required. Fine AP is prepared by

grinding. A vibration ball mill is generally used as a grinding machine. It is not easy to prepare fine AP, of which the particle diameter is less than 20 μm , with a vibration ball mill^{1),2)}. A jet mill is used to prepare fine AP. The jet mill is dangerous for the preparation of fine AP, because fine AP is ignited and exploded easily by slight impact or friction. When fine AP is prepared by a jet mill, it needs special institutions, such as an anti-explosive room, nitrogen atmosphere, impurity removal equipment, etc. Consequently, it is difficult to prepare fine AP particles safely by grinding. Some safe methods of preparing fine AP particles have been developing^{3) 4)}. It is reported that fine AP can be prepared safely by freeze-drying method described below⁵⁾. The procedure is that

Received on December 3, 1999

*Department of Chemistry, National Defense Academy, 1-10-20, Hashirimizu, Yokosuka-shi, Kanagawa, JAPAN
TEL 0468-41-3810 (EXT. 3585)
FAX 0468-44-5901
e-mail kohga@nda.ac.jp

the emulsion with 10m^l toluene and 200m^l AP solution which is frozen rapidly with liquid nitrogen, and the frozen emulsion is freeze-dried. The fine AP prepared by this freeze-drying method was designated as FAP. The mean volume-surface diameter of FAP is about 3.9 μ m⁶⁾. It is expected that the high burning rate AP/HTPB composite propellant could be prepared by 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 prepared from FAP.

2. Experiment

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

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

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 aluminium. The sample weight was about 5mg. The heating rate was 20K/min. The drop hammer test for AP was conducted on the basis of Japanese Explosive Standard ES-21 (1).

HTPB was used as a binder. HTPB was cured with isophorone diisocyanate (IPDI) of a cross-linking agent. IPDI was added to 8wt% of HTPB. The propellant mixtures were cured for 4 days at 333K. The size of each strand was 10mm \times 10mm in cross section and 40mm 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 \pm 1.5K. 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 0.7MPa-7MPa, and was calculated with the cutoff period of two fuses which penetrate the strand at 25mm distance.

3. Results and Discussion

3.1 XRD pattern of AP

It is reported that when the AP solution (100 m^l) saturated at 333K is poured into an organic solvent (300m^l) cooled to 273K, crystal habits of AP recrystallized are modified^{9), 10)}. It was possible that crystal habits of FAP would be modified, because FAP is recrystallized from the emulsion which disperses toluene into AP solution. The crystallographical properties of FAP and GrAP were examined by XRD. When the maximum intensity was identified as 100 on the basis of the measured XRD pattern of FAP or GrAP, the XRD pattern was reillustrated. The XRD patterns of GrAP and FAP are shown in Fig.1. The XRD pattern of FAP is almost the same as that of GrAP. Consequently, it is found that crystal habits of FAP is not modified. The volume fraction of toluene based on AP solution is 0.05. It can be considered that crystal habits of FAP could not be modified, since the added amount of toluene is small.

The crystal defect in AP used was investigated by the Hall's method¹¹⁾. The magnitude of the crystal defect, σ , is represented by the following equation.

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

β is the half width, θ is the Bragg angle of diffraction, λ is the X-ray wavelength and η is the effective particle size. E_{hkl} is the value of Young's modulus for the direction perpendicular to the planes {hkl}. β can be measured from the XRD pattern. When E_{hkl} is assumed to be constant^{10), 12)}, a plot of $\beta \cdot \cos \theta / \lambda$ against $\sin \theta / \lambda$ is linear. From the slope of the straight line,

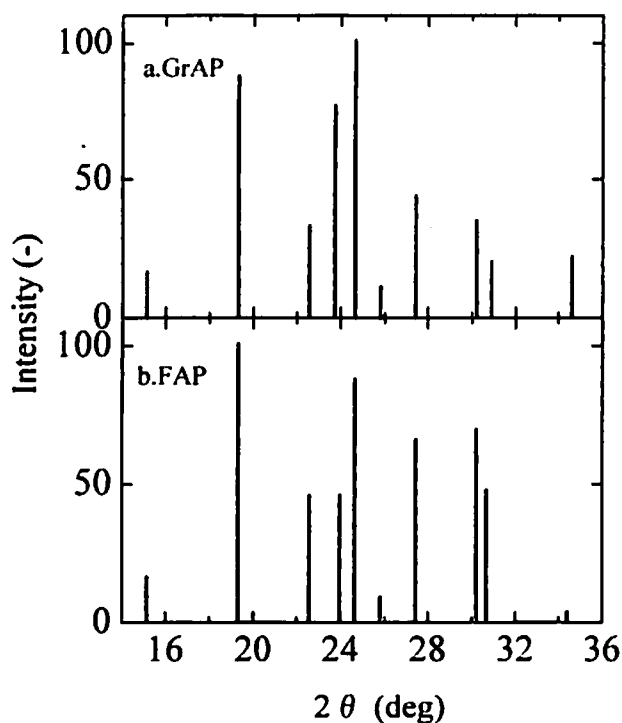


Fig. 1 X-ray diffraction patterns

$2\sigma/E_{hkl}$, that is, σ can be calculated¹⁰⁾⁻¹²⁾. 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 GrAP are approximately zero. This indicates that FAP and GrAP don't develop the crystal defect, even if FAP is recrystallized rapidly by freezing the emulsion with liquid nitrogen and GrAP is ground with the vibration ball mill. It is found that the crystallographical properties of FAP were almost the same as those of GrAP in this study.

3. 2 Thermochemical behavior of AP

For the typical DTA thermogram¹³⁾, the endothermic peak of crystal transformation of AP from orthorhombic to cubic structure is observed at 516K. Subsequently there are two exothermic decompositions, namely, a low temperature decomposition and a high temperature decomposition. For the typical TG thermogram¹³⁾, 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 con-

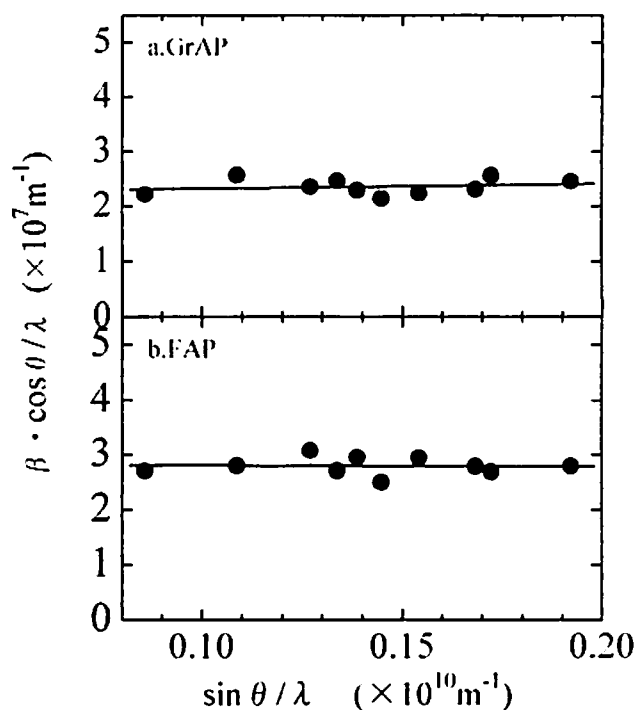


Fig. 2 Relationship between $\beta \cdot \cos \theta / \lambda$ and $\sin \theta / \lambda$

sumption of AP occurs and AP is consumed completely. The DTA and TG thermograms of FAP and GrAP are shown in Fig.3. The DTA and TG thermograms of FAP are almost the same as these thermograms of GrAP, respectively. Fig.3 indicates that thermochemical behavior of FAP and GrAP 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 crystal¹³⁾. As shown in Fig.3, consumption at the low temperature decomposition of FAP and GrAP is a little. This result indicates that a crystal defect of FAP and GrAP is little. This could support the result obtained from XRD pattern.

3. 3 Drop hammer test

The sensitivity of AP on impact increases with decreasing particle size. It's 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. The results of the drop hammer test on FAP and GrAP are shown in Table 1. The sensitivity class of FAP

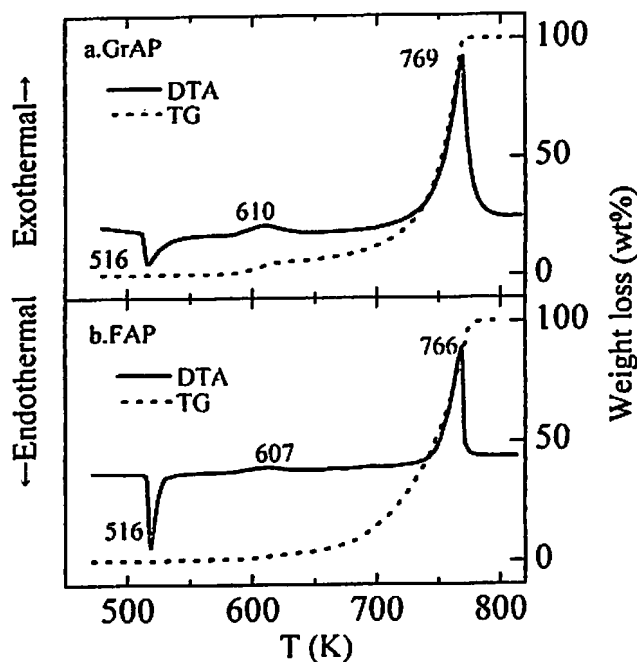


Fig. 3 DTA and TG thermograms

is higher than that of GrAP. 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 Burning rate characteristics

In the preparation of AP/HTPB composite propellant, the uncured propellant is cast into the rocket motor. Therefore it's required that the uncured propellant has suitable viscosity at casting. On the other hand, when the proportion of bubble contamination in AP/HTPB composite propellant is more than 2.0vol%, the burning rate of the propellant is influenced by the bubble contamination and consequently the reproducible burning rate

can't be obtained¹⁴⁾. In order to prepare the propellant, of which the burning rate is reproducible, it is necessary that the proportion of the bubble contamination in the propellant is less than 2.0vol%. Because of the above two requirements for the preparation of AP/HTPB composite propellant, the upper limit content of AP containing propellant, ϕ_{max} (wt%), exists¹⁵⁾. ϕ_{max} was determined by the procedure explained in Ref.15. ϕ_{max} of the propellant prepared from FAP and GrAP was 80wt% and 85wt%, respectively. The propellants containing 80wt%FAP and 85wt% GrAP were designated as Prop.A and Prop.B, respectively. The burning rate characteristics of Props.A and B are plotted in Fig.4. The burning rate of AP/HTPB composite propellant increases with increasing AP content. The AP content of Prop. A is smaller than that of Prop.B, however the burning rate of Prop.A is higher than that of Prop.B. It could be considered that this is because the particle diameter of FAP is much smaller than that of GrAP.

In order to make clear the effect of the AP content on the burning rate, the propellants containing less than ϕ_{max} were prepared and the burning rates were measured. For AP based composite propellant, the burning rate plateaus or mesa is produced by lowering AP content¹⁶⁾. The burning rate of the propellant containing 69wt%FAP is shown plateaus between 6MPa and 8MPa. The burning rate of the propellant containing above 70wt%FAP can follow Vieille's law, that is, neither a plateaus nor a mesa is observed. The burning rate of the propellant containing above 70wt% GrAP can follow Vieille's law. Above 70wt% AP, the relationship between the burning rate at

Table 1 Sensitivity of drop hammer test

Sample	Drop height (cm)	Experimantal results	Sensitivity class
GrAP	40	××××××	7
	45	×○××○×	
FAP	20	××××××	5
	25	○××○××	

○ : explosion, × : non-explosion

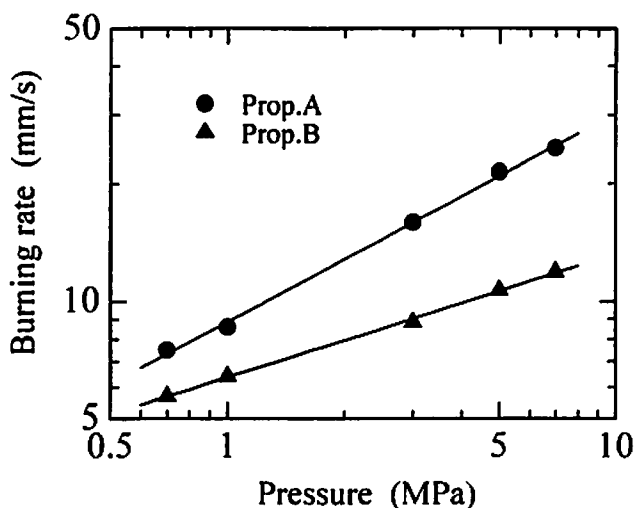


Fig. 4 Burning rate characteristics of Props. A and B

1MPa or 7MPa and the AP content is shown in Fig.5. The burning rate of the propellant prepared from FAP is higher than that of the propellant prepared from GrAP at both pressures. The burning rate increases with increasing the AP content. For GrAP, the increment of the burning rate measured at 7MPa is almost the same as that of the burning rate measured at 1MPa. For FAP, the increment of the burning rate measured at 7MPa is larger than that of the burning rate measured at 1MPa. The increment of the burning rate of the propellant prepared from FAP is larger than that of the propellant prepared from GrAP and increases greatly with coming close to ϕ_{max} , in particular.

The burning rate increases with increasing AP content. It's necessary for the preparation of the higher burning rate AP/HTPB composite propellant to increase the AP content in propellant. As shown in Fig.5, the burning rate increases with increasing the FAP content and the increment of the burning rate increases with coming close to ϕ_{max} . This suggests that the burning rate could be increased greatly by a slight increment of ϕ_{max} of the propellant prepared from FAP. As mentioned above, the propellant containing above 80wt%FAP could not be prepared. At casting, the viscosity of the uncured propellant is almost constant¹⁵⁾. It was expected that ϕ_{max} of the propellant prepared

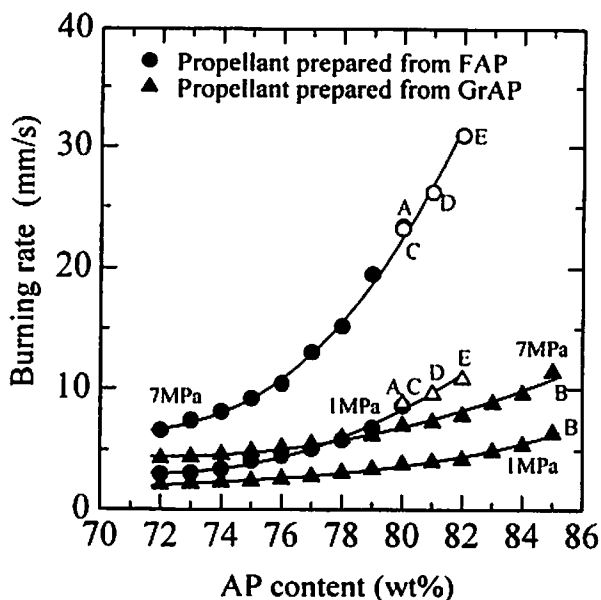


Fig. 5 Relationship between burning rate and AP content (A and B: propellants not added sodium lauryl sulfate, C-D: propellants added sodium lauryl sulfate)

from FAP could be increased, if the viscosity of the uncured propellant could be decreased. It is reported that the viscosity of the uncured propellant can be decreased by adding a surface active agent to HTPB prepolymer¹⁷⁾ and sodium lauryl sulfate, in particular, is largely effective in decreasing the viscosity of uncured propellants. ϕ_{max} of the propellant prepared from FAP and HTPB prepolymer added sodium lauryl sulfate was investigated. The added amount of sodium lauryl sulfate is 0.005 wt% relative to HTPB prepolymer¹⁷⁾. When HTPB prepolymer added sodium lauryl sulfate was used as a binder, ϕ_{max} of the propellant prepared from FAP was 82wt%. By adding sodium lauryl sulfate to HTPB prepolymer, ϕ_{max} of the propellant prepared from FAP can be increased by 2wt%. The burning rate characteristics of the propellants containing 80 and 82wt%FAP by use of HTPB prepolymer added sodium lauryl sulfate are shown in Fig.6. The burning rate of propellant containing 82wt%FAP is reproducible and increases lineally in a plot of $\ln(\text{burning rate})$ versus $\ln(\text{pressure})$. The propellants containing 80, 81 and 82wt%FAP by use of HTPB prepolymer added sodium lauryl sulfate were designated as Prop.C, Prop.D and Prop.E, respectively.

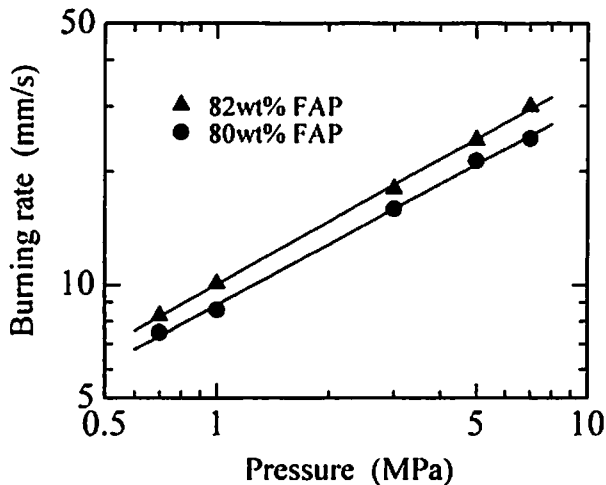


Fig. 6 Burning rate characteristics of propellant from FAP and HTPB prepolymer added sodium lauryl sulfate

The relationships between the burning rate and the FAP content of Props. C, D and E are shown also in Fig. 5. The burning rates of Props. C, D and E are plotted on the extension of the relationship between the burning rate and the FAP content of the propellant prepared from FAP and HTPB prepolymer which did not add sodium lauryl sulfate. The burning rates of Prop. C are almost the same as those of Prop. A. This indicates that the addition of sodium lauryl sulfate did not influence a burning rate in this study. The burning rate measured at 7MPa of Prop. E is 30.1mm/s. The burning rates of Prop. E are higher than those of Props. A or C. This is because the FAP content could be increased by use of HTPB prepolymer added sodium lauryl sulfate.

4. Conclusions

Fine ammonium perchlorate (FAP), of which the mean volume-surface diameter is about $3.9\mu\text{m}$, is prepared by freeze-drying method. The crystallographical property and the thermochemical behavior of FAP, and the burning rate characteristics of the propellant prepared from FAP were investigated in this study. The results were as follows; 1) The crystallographical property and the thermochemical behavior of FAP are almost the same as those of commercial AP. 2) The upper limit content of FAP containing propellant, ϕ_{max} (wt%), was 80wt%. The burning rate measured at 7MPa

of the propellant containing 80wt%FAP is 24.6 mm/s. 3) The burning rate increases with increasing the FAP content. The increment of burning rates at high pressures is larger than that at low pressures, and especially the increment of burning rates increases greatly with coming close to ϕ_{max} . 4) When HTPB prepolymer added sodium lauryl sulfate was used as a binder, ϕ_{max} of the propellant prepared from FAP was 82wt%. By the use of HTPB prepolymer added sodium lauryl sulfate, ϕ_{max} of FAP could be increased by 2wt%. The burning rate measured at 7MPa of the propellant containing 82wt%FAP is 30.1mm/s. It is found that FAP is an effective oxidizer in preparing high burning rate AP/HTPB composite propellant.

References

- 1) Y. Hagihara and T. Ito, "Grinding of Ammonium Perchlorate by Ball Mill", J. Ind. Expl. Soc., 28, 330-334 (1967)
- 2) Y. Hagihara, "Grinding of Ammonium Perchlorate by Vibration Ball Mill", *ibid.*, 43, 70-74 (1982)
- 3) *idem*, "AP-HTPB Composite Propellant Using Freeze-Dried Ammonium Perchlorate Prepared by Method(I)", *ibid.*, 52, 108-114 (1991)
- 4) M. Kohga, M. Suzuki and Y. Hagihara, "Ultra Fine Ammonium Perchlorate Prepared by Freeze-Dry Method", *ibid.*, 53, 295-300 (1992)
- 5) M. Kohga and Y. Hagihara, "The Preparation of Fine Porous Ammonium Perchlorate by the Spray-drying Method", J. Soc. Powder Technol., 33, 273-278 (1996)
- 6) *idem*, "The Preparation of Fine Ammonium Perchlorate by the Spray-drying Method- The Effect of Organic Solvents on the Particle Shape and Size-", *ibid.*, 34, 437-442 (1997)
- 7) *idem*, "The Spray-drying of Ammonium Perchlorate by Ultrasonic Comminution", *ibid.*, 34, 522-527 (1997)
- 8) *idem*, "Preparation of Fine Ammonium Perchlorate by Freeze-Drying", Kagaku Kogaku Ronbunshu, 23, 163-169 (1997)
- 9) Y. Hagihara and T. Ito, "Crystal Habit Modification of Ammonium Perchlorate by Organic Solvents", J. Ind. Expl. Soc., 48, 158-164 (1987)

- 10) Y. Hagihara, M. Kohga, M. Suzuki, H. Tsuzuki and Y. Arakawa, "Crystal Habit Modified Ammonium Perchlorate(1)-Surface properties and thermal decomposition characteristics-", J. Japan Expl. Soc., 58, 237-244 (1997)
- 11) W. H. Hall, "X-ray line broadening in metals", Proc. Phys. Soc., 62A, 741-743 (1949)
- 12) D. Fukuma, S. Miyazaki and H. Okamoto, "High Burning Rate Composite Propellants Composed of Ferrocene Derivative Catalysts and VFAP(II)", J. Japan Expl. Soc., 55, 17-23 (1994)
- 13) H. Osada and E. Sakamoto, "Thermal Decomposition of Ammonium Perchlorate", J. Ind. Expl. Soc., 24, 236-244 (1963)
- 14) T. Yamaya, A. Iwama and H. Tokui, "Combustion and Detonation of Porous Composite Propellants(1) Microspheres included Propellant", *ibid.*, 43, 381-386 (1982)
- 15) M. Kohga and Y. Hagihara, "Experimental Study on Estimation of Upper Limit of Ammonium Perchlorate Content in Ammonium Perchlorate / Hydroxyl-Terminated Polybutadiene composite Propellant", Trans. Japan Soc. Aero. Space Sci., 41, 74-78 (1998)
- 16) J. A. Steinz, P. L. Stang and M. Summerfield, "The Burning Mechanism of Ammonium Perchlorate-Based Composite Propellants", Aerospace and Mechanical Science Report No.830 (1969)
- 17) M. Kohga and Y. Hagiara, "Effects of Addition of Surfactants on Viscosity of Uncured Ammonium Perchlorate / Hydroxyl -Terminated Polybutadiene Propellant", J. Japan Expl. Soc., 58, 167-173 (1998)

凍結乾燥法で調製された微粒過塩素酸アンモニウムを用いた
AP/HTPB系コンポジット推進薬(第4報)

— トルエンとAP水溶液のエマルジョンから調製された
微粒APの場合 —

甲賀 誠*, 萩原 豊*

凍結乾燥法によって、体面積平均径 $3.9\mu\text{m}$ の微粒な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。1) FAPの結晶学的性質と熱分解性は、市販のAPのそれとほぼ同じであった。2) 推進薬に混入できるFAP有率の上限界($\phi_{max}[\text{wt}\%]$)は80wt%であった。FAP含有率80wt%で製造された推進薬の燃焼速度は24.6mm/s(7MPa)であった。3) FAPを用いた推進薬の燃焼速度は、FAP含有率の増加にしたがい大きくなった。FAP含有率に対する燃焼速度の増加率は、燃焼圧力の増加にしたがい大きく、また ϕ_{max} に近づくほど大きくなった。4) バインダとして用いた末端水酸基ポリブタジエンにラウリル硫酸ナトリウムを添加することによって、 ϕ_{max} を82wt%に増加できた。FAP含有率82wt%で製造された推進薬の燃焼速度は30.1mm/s(7MPa)であった。 ϕ_{max} をわずかに増加させることで、燃焼速度を大きく増加できた。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 化学教室 〒239-8989 横須賀市走水1-10-20)