Article

Estimation of highest burning rate of AP/HTPB composite propellant with experimental approach (I)

– Burning rate characteristics of AP/HTPB composite propellant –

Makoto Kohga* and Yutaka Hagihara*

The burning rate is one of the important properties of the propellant. The upper limit content of AP incorporated in AP/HTPB composite propellant, ϕ_{max} exists because of the requirements for the preparation of propellant. The burning rate increases with increasing the AP content and the burning rate of the propellant prepared at ϕ_{max}, r_{ϕ} is the highest value of the propellant prepared with AP used as an oxidizer. It is necessary for the design of AP/HTPB composite propellant to estimate r_{ϕ}. This paper is one of a series of the study to develop the estimation of r_{ϕ} with the experimental approach.

A lot of propellants were prepared with many kinds of AP samples, e.g. spherical AP, porous AP, hollow AP, narrow distribution, wide distribution, monomodal, bimodal, etc., and the burning rate characteristics of the propellants were investigated. The ϕ_{max} of the propellant prepared in this study is in the range of 72 to 85 wt% AP. And the range of r_{ϕ} at 7 MPa is 11.7–25.2 mm·s^{-1}. The increment of burning rate increases remarkably with coming close to ϕ_{max}. The increasing ratio of the burning rate upon the AP content increases with increasing specific surface area less than 500 m^2·kg^{-1}, and is the maximum and almost constant above that. The increasing ratio of the burning rate upon the specific surface area increases linearly with the AP content. The burning rate would be changed greatly by the slight variation of the specific surface area at the higher AP content.

1. Introduction

For the design of a composite propellant, the specific impulse and the burning rate are the important properties. The specific impulse is a physical quantity represents the total impulse per unit weight of propellant. As the burning rate increases, the amount of combustion gas per unit time increases and larger thrust can be obtained. Therefore, a high specific impulse and high burning rate propellant is required.

Ammonium perchlorate (AP) / hydroxyl - terminated polybutadiene (HTPB) composite propellant was adopted in this study because AP/HTPB composite propellant is the most widely used one at present. The specific impulse and the burning rate of AP/HTPB composite propellant increase with increasing AP content. The propellant prepared at the larger AP content is required to obtain the higher specific impulse and the higher burning rate of AP/HTPB composite propellant. The upper limit content of AP incorporated in propellant, ϕ_{max} exists because of the requirements for the preparation of AP/HTPB composite propellant[1,2]. The specific impulse and the burning rate of the propellant at ϕ_{max} are the highest value of the propellant prepared with AP used as an oxidizer. It is necessary for the design of AP/HTPB composite propellant to estimate the specific impulse and the burning rate of the propellant prepared at ϕ_{max}.

It was presented that ϕ_{max} can be estimated with the specific surface area, S_w measured by air-permeability method[2]. The specific impulse can be calculated from the AP content by the thermodynamic method theoretically[3]. Therefore, the specific impulse of the propellant prepared at ϕ_{max} can be estimated by S_w of AP. On the other hand, the burning rate is dependent on the AP content.

Received : May 19, 2003
Accepted : June 19, 2003
*Department of Applied Chemistry, National Defense Academy, 1-10-20, Hashirimizu, Yokosuka-shi, Kanagawa, 239-8989, JAPAN
TEL +81-46-841-3810 (ext. 3585)
FAX +81-46-844-5901
E-Mail kohga@nda.ac.jp

However, the burning rate of the propellant prepared at ϕ_{max}, r_ϕ cannot be determined by ϕ_{max} only because the burning rate is not only depend on the AP content but also the particle properties of AP. Now r_ϕ is determined by the measurement of the burning rates of many propellant samples practically. The determination of r_ϕ takes labour and time. It is an important subject for the design of AP/HTPB composite propellant to make the estimation of r_ϕ.

The burning rate characteristics of AP/HTPB composite propellant have been investigating. However, the burning rate characteristics of the propellant prepared at ϕ_{max}, that is, r_ϕ have little been published to date. Many kinds of AP samples, e.g. spherical AP, porous AP, hollow AP, narrow distribution, wide distribution, monomodal, bimodal, etc., were used as an oxidizer in this study. The burning rate characteristics of the propellants prepared with these AP samples were investigated in order to find out the estimation of r_ϕ with the experimental approach. This paper is one of a series of the study to estimate r_ϕ.

2. Experimental

2. 1 Samples

AP samples used in this study are shown in Table 1. Samples A−E were prepared by grinding commercial AP for 5, 10, 20, 30 and 40 minutes in a vibration ball mill. Sample F was prepared by shifting sample E and

Table 1 Formulation of propellant prepared with bimodal AP

Symbol	Sample	shape	D_{vs} (μm)	S_w ($m^2 \cdot kg^{-1}$)
A	AP ground in vibration mill for 5 minutes	Spherical	110	40
B	AP ground in vibration mill for 10 minutes	Spherical	70	50
C	AP ground in vibration mill for 20 minutes	Spherical	50	100
D	AP ground in vibration mill for 30 minutes	Spherical	40	150
E	AP ground in vibration mill for 40 minutes	Spherical	40	180
F	38 μm passed	Spherical	20	260
G	AP prepared by the spray-drying method	Spherical	2	1010
H	AP prepared by the spray-drying method	Spherical	2	940
I	AP prepared by the spray-drying method	Spherical	3	900
J	AP prepared by the spray-drying method	Porous	6	1060
K	AP prepared by the spray-drying method	Porous	8	450
L	AP prepared by the spray-drying method	Porous	7	780
M	AP prepared by the spray-drying method	Porous	4	840
N	AP prepared by the spray-drying method	Porous	3	990
O	AP prepared by the spray-drying method	Porous	4	860
P	AP prepared by the spray-drying method	Hollow	3	1200
Q	AP prepared by the spray-drying method	Hollow	3	1160
R	AP prepared by the freeze-drying method	Hollow	4	610
S	AP prepared by the freeze-drying method	Hollow	11	370
a	A:G=20 wt%:80 wt%		2	480
b	A:J=40 wt%:60 wt%		10	470
c	A:P=50 wt%:50 wt%		5	550
d	A:R=60 wt%:40 wt%		9	220
e	A:R=40 wt%:60 wt%		6	310
f	G:R=80 wt%:20 wt%		2	820
g	G:R=60 wt%:40 wt%		2	690
h	G:R=50 wt%:50 wt%		2	630

was AP particles passed 38 μm. Sonic sifter was used as a sifter. Samples G−Q were prepared by the spray-drying method[1-6]. Samples R and S were prepared by the freeze-drying method[7]. Samples a−h were the mixture of two AP samples.

The scanning electron microscope (SEM) photographs of samples A, J, P, and R are shown in Figure 1. The shape and the mean volume-surface diameter on number basis, D_{vs} of AP sample were examined from SEM photograph. The results are shown in Table 1. The D_{vs} is in the range of 2 to 110 μm. The shape of samples A−E was spherical and the particle size distribution was wide. The shape of sample F was spherical and the distribution was narrow. The shapes of samples G−I, samples J – O, and samples P−S were spherical, porous, and hollow, respectively. These particle size distributions were narrow. According to the external view of sample J, porous AP has some small holes at the shell and the void inside the porous AP particle is connected to outside the particle. The shape of samples P and R looks spherical according to the SEM photograph. However, these samples have a void at the particle, that is, hollow[6,7]. Samples a−h were bimodal. The S_w was determined in Ref.2. The result was shown in Table 1. The range of S_w is 40 − 1200 $m^2 \cdot kg^{-1}$.

Differential thermal analysis (DTA), thermogravimetry (TG) and X-ray diffractometry (XRD) were employed as preliminary experiment. The DTA-TG thermograms and the XRD patterns of AP shown in Table 1 were almost the same and were closely coincided with the typical DTA-TG thermogram and XRD pattern of AP, respectively. These results indicate that the thermochemical behavior and the crystallographical properties of AP used in this study were almost the same.

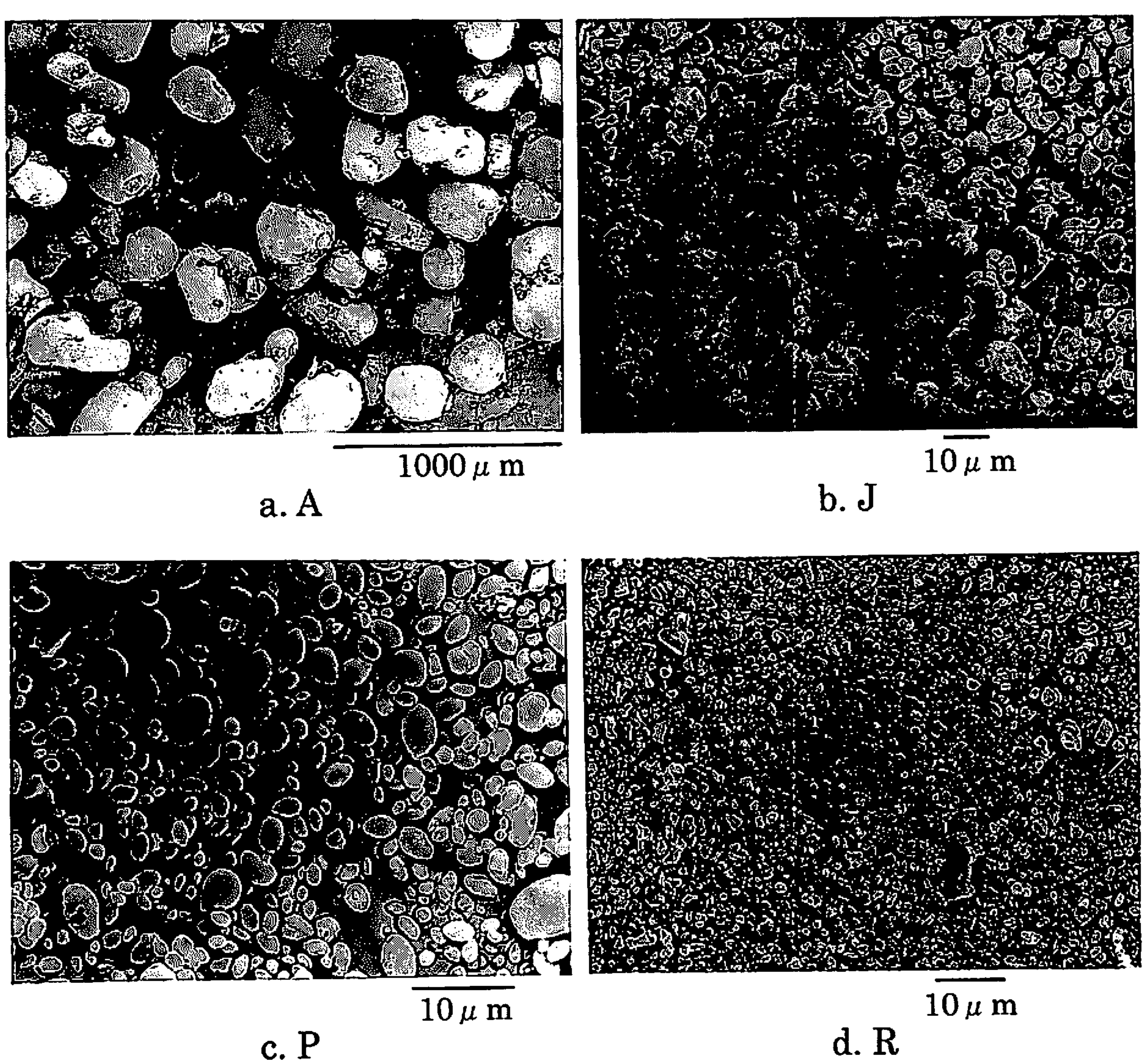

Fig.1 SEM photographs of samples A, J, P, and R

HTPB R-45M was used as a binder. HTPB was cured with isophorone diisocyanate. Isophorone diisocyanate was added to 8 wt% of HTPB.

In order to determine ϕ_{max} and r_0, a propellant should be prepared with the optimum operating condition. The optimum operating condition in this study was decided on the basis of the results of Ref.8 and the propellant samples were prepared according to Refs. 1 and 2.

The AP/HTPB propellant samples prepared were designated by the symbols of AP sample. For example, the propellant sample prepared with sample A was designated as propellant A.

2. 2 Measurement of burning rate

The burning rate was measured in a chimney type strand burner which was pressurized with nitrogen at 288 ±1.5 K. The range of pressure was from 0.5 MPa to 7 MPa. The strand sample was ignited by an electrically heated nichrome wire attached on the top of each strand sample. Two fuse wires were threaded through the strand sample at 25 mm distance. The fuse wire was cut as soon as the burning surface passed through the fuse wire. The burning rate was calculated with the cutoff period of two fuses.

3. Results and Discussion

3. 1 Propellant prepared at ϕ_{max}

The ϕ_{max} exists owing to the requirements for the preparation of AP/HTPB composite propellant[1,2]. The burning rate increases with increasing the AP content and r_0 is the highest value of the propellant prepared with AP used as the oxidizer. The r_0 can be determined inevitably at the same time as the decision of ϕ_{max}.

The ϕ_{max} was determined in the following way experimentally according to Refs.1 and 2. 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% AP 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 and the relationship between burning rate and pressure follows Vieille's law according to the experience in this laboratory. When the burning rate is reproducible and 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, ϕ_{max} was determined as the largest AP content in the propellants, of which the burning rate is not influenced by the bubble contamination.

The propellants were prepared with AP samples shown in Table 1 and the burning rates of their propellants were measured. Figure 2 shows the burning rate characteristics of propellants A, J, P, and R. The burning rate increases with increasing AP content. The propellant prepared above certain AP content could not obtain reproducible burning rates. The largest AP contents to obtain the reproducible burning rate for propellants A, J, P, and R are 85, 73, 72, and 80 wt% AP, respectively. This result indicates that the values of ϕ_{max} for propellants A, J, P, and R are 85, 73, 72, and 80 wt% AP, respectively. The ϕ_{max} of the propellants prepared with AP samples shown in Table 1 were determined in the same way as above mentioned The results are shown in Table 2. The ϕ_{max} is in the range of 72 to 85 wt% AP. The ϕ_{max} of propellants A and B is the maximum, 85 wt% AP, and that of propellants P and Q is the minimum, 72 wt% AP, in this study.

The plot of log(burning rate) against log(pressure) is found to be approximately linear. The r_0 at certain pressure could be estimated almost exactly by the straight

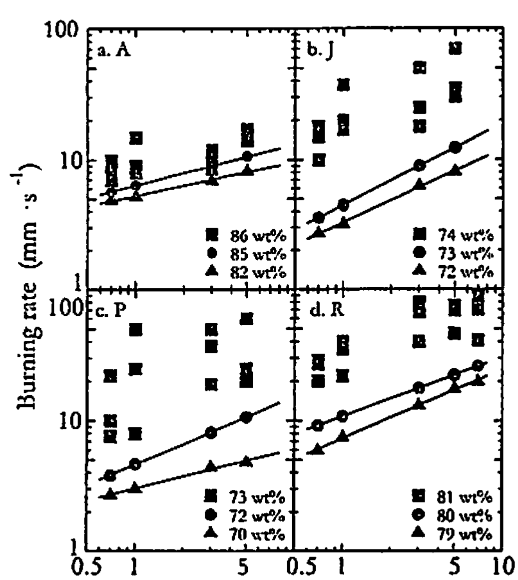

Fig.2 Burning rate characteristics of propellants A, J, P, and R

line drawing with two points on a log(burning rate) – log(pressure) graph. The r_ϕ measured at 1 MPa or 7 MPa was determined from the burning rate characteristics as shown in Fig.2. These values are also shown in Table 2. The ranges of r_ϕ at 1 MPa and 7 MPa are 4.7–9.3 $mm \cdot s^{-1}$ and 11.7 – 25.2 $mm \cdot s^{-1}$, respectively. The r_ϕ at 7 MPa of the propellant g is the highest in this study.

3. 2 Increasing ratio of burning rate

3. 2. 1 Increasing ratio upon AP content

The burning rate increases as the AP content increases. In order to make clear the effect of the AP content on the burning rate, the relationship between the burning rate measured at 1 MPa or 7 MPa and the AP content is shown in Figure 3. The burning rate increases with increasing AP content and especially the increment of the burning rate increases greatly with coming close to ϕ_{max}. The increment of the burning rate measured at 7 MPa is larger than that of the burning rate measured at 1 MPa. These relationships differ from one another and the increment of the burning rate is varied with AP sample. This result suggests that the influence of the AP content on the burning rate would be dependent on the particle properties of AP.

The increasing ratio of the burning rate upon the AP content, α is defined as the following.

$$\alpha = \frac{dr}{d(AP\ content)}$$

As mentioned above, the increment of burning rate increases remarkably in the vicinity of ϕ_{max}. In order to make clear the difference in α, α was determined

Table 2 Burning rate characteristics

Symbol	ϕ_{max} (wt%)	r_ϕ ($mm \cdot s^{-1}$)		α (-)
		1 MPa	7 MPa	
A	85	5.3	11.7	1.7
B	85	5.3	12.1	1.9
C	84	5.4	12.4	2.1
D	83	5.4	12.8	2.6
E	83	5.5	14.2	3.1
F	82	5.7	15.1	3.5
G	75	6.2	16.9	4.6
H	76	6.9	19.8	4.7
I	77	7.2	21.8	4.3
J	73	5.8	15.4	5.2
K	80	6.9	19.1	4.5
L	77	7.4	24.2	5.5
M	77	7.1	23.1	4.5
N	74	6.2	17.2	5.1
O	76	7.1	21.1	4.8
P	72	4.7	13.1	5.0
Q	72	5.2	12.2	4.7
R	80	9.3	24.6	4.9
S	81	7.5	19.5	5.2
a	80	7.2	20.5	4.7
b	80	7.3	19.8	4.9
c	80	8.9	22.8	4.5
d	83	5.9	13.5	3.0
e	82	6.2	14.2	3.5
f	78	7.2	22.2	5.2
g	79	8.9	25.2	5.1
h	79	9.1	25.1	5.4

from the difference between r_0 and the burning rate of the propellant prepared at the AP content which subtract 1 wt% from ϕ_{max}. The α calculated by use of the burning rate measured at 7 MPa is larger than that at 1 MPa. The α calculated from the burning rate at 7 MPa was used in the following discussion. The values of α are shown in Table 2. The range of α is 1.7−5.5.

The flame of AP composite propellant is a so called diffusion flame, and the model of Multiple Flames[9] is generally accepted as a model of the flame structure. According to the model of Multiple Flames, the oxidizer and binder decomposition products diffuse and mix and, consequently, the combustion occurs. It can be considered that the combustion of AP occurs on the surface of AP particle. Some porous or hollow AP samples were used in this study. This suggested that S_w would be an appropriate property to express the surface area of AP particle contributes to the combustion, compared with D_m. The S_w was used as the particle property to represent the size of AP particle relates to combustion in following discussion. Figure 4 shows the influence of α on S_w. The α increases with increasing S_w less than 500 $m^2 \cdot kg^{-1}$, and is the maximum and approximately constant above that. This fact indicates that for the propellant prepared with AP, of which S_w is above 500 $m^2 \cdot kg^{-1}$, the increment of the burning rate in the vicinity of ϕ_{max} is the maximum and almost constant.

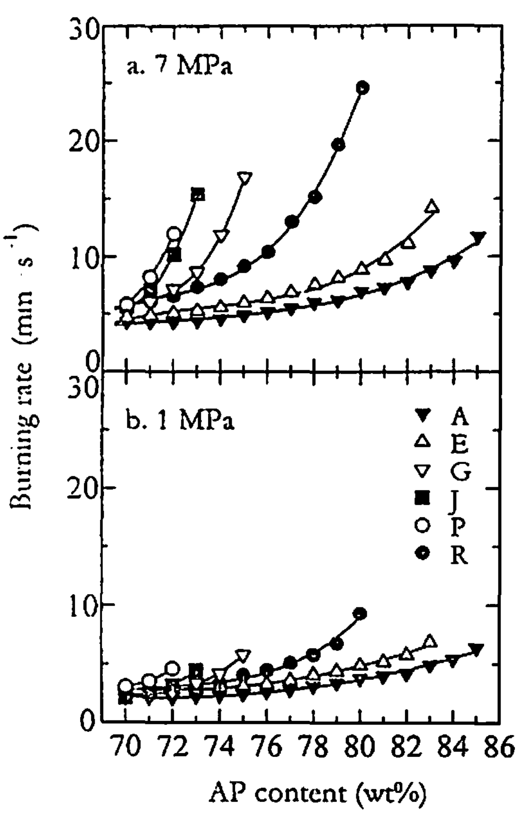

Fig.3 Relationship between burning rate and AP content

3. 2. 2 Increasing ratio upon S_w

The burning rate depends not only on the AP content but also on the particle properties of AP, e.g. particle diameter and specific surface area. The S_w was adopted as the particle property to represent the size of AP particle contributes to the combustion as mentioned in section 3.2.1. The increasing ratio of the burning rate upon S_w, β was examined in this section.

Figure 5 shows the relationship between the burning

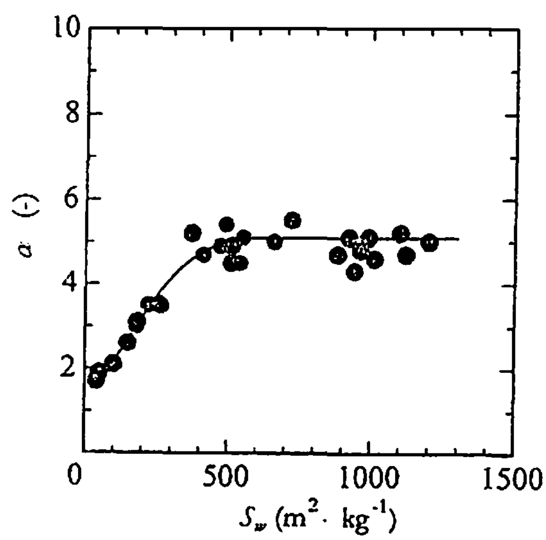

Fig.4 Influence of Sw on α

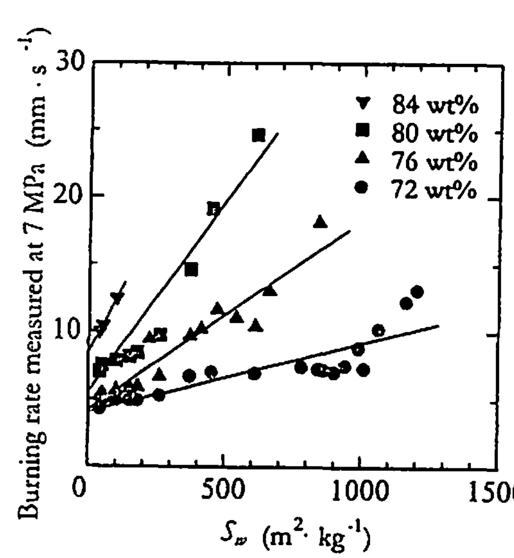

Fig.5 Relationship between burning rate at 7 MPa and Sw

Table 3 Results of β

AP content (wt%)	β (-)
72	0.0046
73	0.0061
74	0.0094
75	0.0113
76	0.0163
77	0.0182
78	0.0215
79	0.0240
80	0.0274
81	0.0298
82	0.0334
83	0.0364
84	0.0376
85	0.0400

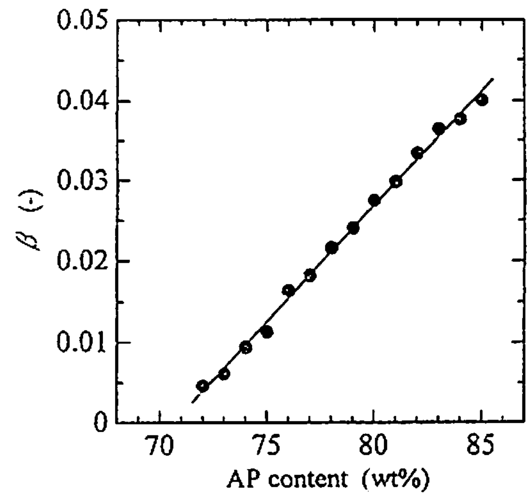

Fig.6 Influence of AP content on β

rate measured at 7 MPa and S_W. The burning rate increases with increasing S_W. The approximate equation was determined by the least squares method and was expressed by a solid line in Fig.5. These relationships follow a straight line approximately. The slope of the straight line is β. The values of β are also shown in Table 3. The range of β is 0.0046−0.0400. Fig.6 shows the influence of β on the AP content. The β increases linearly with the AP content. This result suggested that the burning rate would be changed greatly by the slight variation of S_W at the higher AP content.

4. Conclusions

The upper limit content of AP incorporated in AP/HTPB composite propellant, ϕ_{max} exists because of the requirements for the preparation of propellant. The burning rate increases with increasing AP content and the burning rate of the propellant prepared at ϕ_{max}, r_0 is the highest value of the propellant prepared with AP used as an oxidizer. It is necessary for the design of AP/HTPB composite propellant to estimate r_0. In this study, the burning rate characteristics of AP/HTPB composite propellant were investigated in order to develop a estimation of r_0 with the experimental approach. The following results were obtained : 1) The ϕ_{max} of the propellant prepared in this study is in the range of 72 to 85 wt% AP. The range of r_0 at 7 MPa is 11.7 – 25.2 mm·s^{-1}. 2) The increment of burning rate increases remarkably with coming close to ϕ_{max}. The increasing ratio of the burning rate upon the AP content increases with increasing specific surface area less than 500 m^2·kg^{-1}, and is the maximum and almost constant above that. 3) The increasing ratio of the burning rate upon the specific surface area increases linearly with the AP content. The burning rate would be changed greatly by the slight variation of the specific surface area at the higher AP content.

The estimation of r_0 will be discussed on the basis of these results and the details will be presented in a subsequent paper.

References

1) 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 (132), 74-78 (1998).

2) idem," Estimation of Upper Limit of AP Content in AP/HTPB Composite Propellant -A consideration based on Flow Characteristics of AP/HTPB ", J. Ind. Expl. Soc., Japan, 61 (4), 157-166 (2000).

3) S. Gordon and B. J. MacBrige, " Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouget Detonations ", NASA SP-273, NASA Lewis Research Center, Interim Revision, (1976).

4) M. Kohga and Y. Hagihara;" The Preparation of Fine Porous Ammonium Perchlorate by the Spray-drying Method", J. Soc. Powder Technol., Japan, 33(4), 273-278 (1996).
5) idem;" The Preparation of Fine Porous Ammonium Perchlorate by the Spray-drying Method －The Effect of Organic Solvents on the Particle Shape and Size －", ibid., 34(6), 437-442 (1997).
6) idem;" The Spray-drying of Ammonium Perchlorate by Ultrasonic Commination", ibid., 34(7), 522-527 (1997).
7) idem;" Preparation of Fine Ammonium Perchlorate by Freeze-Drying", Kagaku Kougaku Ronbunshu, 23 (2), 163-169 (1997).
8) idem;" Experimental Study on Operating Conditions for Preparation of Ammonium Perchlorate/Hydroxyl-Terminated Polybutadiene Composite Propellant(I) －Influences of Temperature on Viscosity of Uncured Propellant－", J. Expl. Soc., 59(1), 1-5 (1998).
9) M. W. Beckstead, R. L. Derr and C. F. Price;" A Model of Composite Solid- Propellant Combustion Based on Multiple Flames", AIAA J., 8(12), 2200-2207 (1970).

実験的手法によるAP/HTPB系コンポジット推進薬の最高燃焼速度の推算(I)
－AP/HTPB系コンポジット推進薬の燃焼速度特性－

甲賀　誠*，萩原　豊*

AP/HTPBコンポジット推進薬は製造上の条件があるために，推進薬中に混入できるAP含有率の上限，ϕ_{max}がある。推進薬の燃焼速度は，AP含有率の増加にしたがい大きくなり，ϕ_{max}で製造された推進薬の燃焼速度，r_cは最大値となる。推進薬を設計する上で，r_cを推算することは必要である。実験的な手法によってr_cの推算法を見いだすために，AP/HTPBコンポジット推進薬の燃焼特性を調べた。本実験は，r_cの推算法を見いだすための一連の実験の一つである。

さまざまな粒子径(体面積平均径：2－110 μm)，粒子形状(球状，多孔質，中空)，比表面積(40－1200 $m^2 \cdot kg^{-1}$)，粒度分布(一山分布，二山分布)のAPを用いることによって，ϕ_{max}が72－85 wt%AP，7 MPaにおけるr_cが11.7－25.2 $mm \cdot s^{-1}$の推進薬を製造できた。製造された推進薬の燃焼速度はAP含有率の増加にしたがい大きくなり，特にϕ_{max}近傍における燃焼速度増加率は大きいことがわかった。AP含有率の増加による燃焼速度増加率は，比表面積が500 $m^2 \cdot kg^{-1}$以下では比表面積の増加にしたがい大きくなり，それ以上ではほぼ一定で最大値となった。比表面積の増加による燃焼速度増加率は，AP含有率の増加にしたがい直線的に大きくなった。このことは，AP含有率が大きくなるほど，APの比表面積がわずかに変化すれば，燃焼速度は大きく変化することを示している。

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