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Burning-Rate Characteristics of Composite Propellant Using Ammonium Perchlorate Modified by Ethylene Glycol

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Ammonium perchlorate (AP)-based composite propellants are currently the most widely used type of propellant. AP composite propellants with high burning rates are desirable for many applications. In this study, hexahedral crystal-habit-modified AP was prepared from ethylene glycol. Modified AP possessed a remarkably intense lattice plane (210) due to the magnitude of crystal habit modification in AP. Thermal decomposition and ignition behavior of modified AP was superior to those of standard AP. The burning rate of propellant containing modified AP was higher than propellant with standard AP. The effect of crystal habit modification on burning rate was dependent on the extent of modification. Results of this study revealed that crystal-habit-modified AP prepared with ethylene glycol was an effective oxidizer that enhanced the burning rate of AP-based composite propellants.

Nomenclature

B_r = ratio of burning rates
D_w = weight mean diameter, μm
E = activation energy, kJ/mol
R = gas constant
T = temperature, K
t = ignition delay period, s
λ = wavelength, m
θ = angle of diffraction, degree
ξ = ratio of (210) plane intensity to total intensity of each main peak in x-ray diffractometry patterns

I. Introduction

COMPOSITE propellants are a class of solid or heterogeneous rocket propellants consisting of a large amount of powdered oxidizer held together in a matrix of synthetic rubber or a plastic binder. Ammonium perchlorate (AP) has been widely used as an oxidizer, and hydroxyl-terminated polybutadiene (HTPB) has been used as a binder. Propellants with a high burning rate that generate a large quantity of combustion gases in a short period of time are required to obtain high-performance rocket motors, enabling rockets to fly at high speeds. Therefore, many studies have been directed towards the development of propellants with high burning rates.

The burning rate of an AP-based composite propellant increases with a decrease in AP diameter and an increase in AP content. Fine AP particles are required to obtain AP-based composite propellants with a high burning rate. AP particles approximately 20 μm in diameter can be prepared by standard grinding methods, such as vibration ball milling. However, finer AP particles are difficult to prepare using this method [1,2]. Jet mills, which use compressed air or gas to produce fine particles, are able to produce AP particles finer than 20 μm in diameter. However, jet milling is dangerous because fine AP particles may ignite and explode upon slight impact or friction. To prepare fine AP particles using a jet mill, special facilities are required that have an anti-explosive room, a nitrogen atmosphere, equipment to remove impurities, and so on. While it is not easy to safely prepare fine AP particles with a mechanical grinding method, some methods based on spray-drying and freeze-drying have been conducted [3–8].

Specific impulse and burning rate are among the most important parameters affecting the performance of propellants. High specific impulse is required for enhanced propellant performance and increases with increasing AP content. The burning rate of an AP-based propellant also increases with increasing AP content. Overall, AP/HTPB composite propellants prepared with high amounts of fine AP possess a high specific impulse and burning rate.

In the preparation of an AP/HTPB composite propellant, AP is mixed with HTPB and curing agent. The resultant AP/HTPB slurry is cast into a rocket motor. Thus, AP/HTPB slurry must possess a viscosity suitable for casting. On the other hand, a reproducible burning rate cannot be obtained if bubble contamination in AP/HTPB composite propellants is more than 2.0 vol% [9]. To prepare a propellant with a burning rate that is not affected by bubble contamination, it is necessary to limit contamination to less than 2.0 vol%. Because of aforementioned requirements, the amount of AP that can be incorporated into a propellant is limited [10,11]. Additionally, the upper limit of AP content decreases with a decrease in AP particle size. Although a propellant with a high burning rate can be obtained with fine AP particles, the specific impulse of the propellant decreases with particle size.

Ito and Hikita [12], Hagihara and Ito [13], and Hagihara et al. [14] reported that the crystal habit of AP was modified by the addition of specific organic solvents and surfactants. Additionally, modified APs were found to be effective oxidizers in composite propellants [15]. Figure 1 shows an SEM photograph of crystal-habit-modified AP, revealing that a majority of the particles are dendritic. Because of preparation requirements for AP/HTPB composite propellants, there is an upper limit on the amount of AP that can be incorporated into a propellant [10,11]. The viscosity of an uncured propellant based on modified APs is high during mixing and casting due to the dendritic shape of modified APs. A propellant with an AP content above 73.5% could not be prepared with dendritic-modified AP [15]. Thus, the upper limit of dendritic-modified AP that can be incorporated into an AP/HTPB propellant was low.

AP/HTPB slurry had a favorable mixing and casting viscosity when AP particles in the shape of spheres or polygons were used as an oxidizer. Therefore, the upper limit of spherical or polygonal AP that can be incorporated in a propellant is larger than dendritic AP.

Hexahedral crystal-habit-modified AP was prepared with ethylene glycol [16]. In general, hexahedral-modified AP is expected to be an effective oxidizer and enhance the burning rate of an AP-based composite propellant. Crystallographic and particle properties of hexahedral-modified AP have been reported [16]. However, thermal decomposition behavior of hexahedral-modified AP has not been

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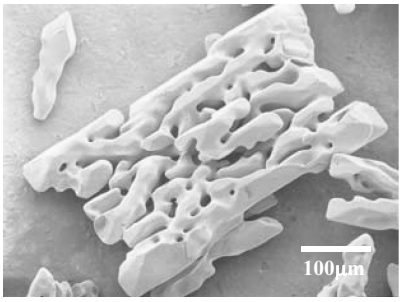


Fig. 1 SEM photograph of crystal-habit-modified AP possessing a dendritic shape with *n*-butyl alcohol as an organic solvent.

studied. In this investigation, thermal decomposition behavior of hexahedral crystal-habit-modified AP and the burning rate of propellants containing modified AP were investigated.

II. Experimental

A. Preparation of crystal-habit-modified AP

Hexahedral crystal-habit-modified AP was prepared by the method described below [16]. Figure 2 shows the preparation of hexahedral crystal-habit-modified AP. Ethylene glycol was used as a crystal habit modifier for AP. Modified AP was prepared by recrystallization from an aqueous ethylene glycol solution saturated with AP. The mass ratio of ethylene glycol to distilled water was 80/20 in this study because the yield of the modified AP was relatively high. The aqueous ethylene glycol solution (ethylene glycol/water = 80/20) saturated with AP is referred to as the saturated AP solution hereafter.

Aqueous ethylene glycol solutions at 273 and 333 K were prepared and AP was added to obtain a saturated solution at each temperature. 200 cm^3 of saturated AP solution at 333 K was heated to 338 K in a hot bath and was immediately poured into 2000 cm^3 of a solution at 273 K.

The time required to transfer the solution at 333 K to a solution at 273 K was approximately 10 s. During this time, AP recrystallized from the saturated solution at 333 K due to a decrease in temperature. Saturated AP solutions were subsequently heated to 338 K to prevent recrystallization of AP during the transfer process. Upon cooling to 273 K, AP was recrystallized from a mixed solution.

Recrystallized AP was collected by suction filtration and dried in a vacuum thermostat at 333 K and less than 20 Pa for 6 h. The boiling point of ethylene glycol at 20 Pa was 291 K; thus, residual ethylene glycol was removed during the drying process.

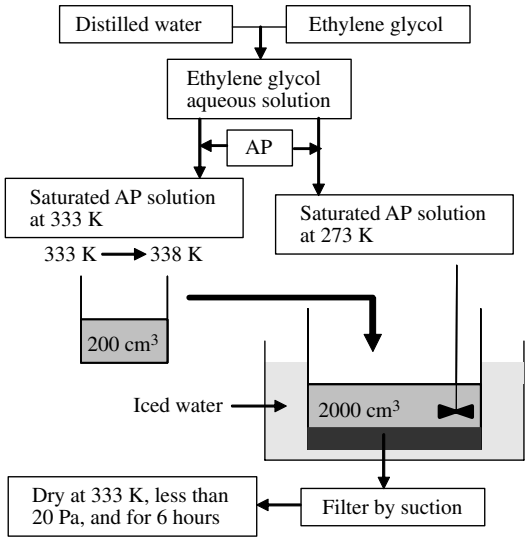


Fig. 2 Preparation of hexahedral crystal-habit-modified AP.

AP prepared with aqueous ethylene glycol is designated as EAP. To compare thermal decomposition behavior, an AP sample was prepared in aqueous solution without ethylene glycol and burning-rate characteristics of the resultant propellant were determined. AP obtained from aqueous solution is designated as NAP.

Scanning electron microscopy (SEM) was used to observe prepared AP. Crystallographic properties of AP were examined by x-ray diffractometry (XRD) with Cu-K_α at a $\lambda = 1.5418 \times 10^{-10}$ m.

B. Measurement of Thermal Decomposition Behavior

Thermochemical decomposition behavior was investigated by differential thermal analysis (DTA) and thermogravimetry (TG). The equipment used in both experiments was operated under a flow of nitrogen (50 mL/min) at atmospheric pressure. Sample containers were made of aluminum and the heating rate was 20 K/min.

C. Ignition Temperature Test

Ignition temperature tests were conducted to investigate temperature sensitivity and thermal behavior due to rapid heating. Tests were performed according to Explosives Society Standards-11 [17]. A Krupp ignition point test rig, consisting of a steel cylinder, was heated in an electric furnace until the temperature increased to approximately 870 K. Thereafter, rig temperature decreased at a rate of less than 2 K/min. 20 mg samples were placed in the rig and ignition delay times were measured at each 2 K decrease in temperature.

D. Measurement of Burning Rate

A propellant was prepared with 80% AP because burning-rate characteristics of this propellant are well-documented. Hydroxyl-terminated polybutadiene (HTPB) was used as a binder and was cured with 8% isophorone diisocyanate.

Each propellant strand was 10 mm in diameter and 40 mm in length. Burning rate was measured in a chimney-type strand burner pressurized with nitrogen at 290 K. Ignition of each strand was achieved by an electrically heated nichrome wire attached to the top of each strand. Burning rate was measured at a pressure of 0.5–7 MPa and was calculated as the cutoff period of two fuses that penetrated the strand at a distance of 25 mm.

III. Results and Discussion

A. AP Samples

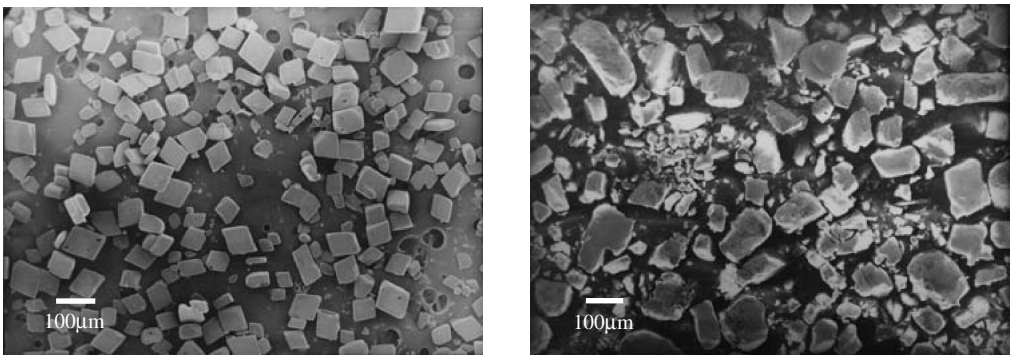
1. *Particle Properties*

Figure 3 shows SEM images of EAP and NAP samples. The EAP samples were almost entirely hexahedral, while the NAP samples were not uniform in shape. The particle sizes of the AP samples were measured using Feret's diameter from the SEM images. Figure 4 shows the particle size distributions of the EAP and NAP samples. The size distribution of the EAP samples was bimodal; two peaks were observed at 80 and 140 μm. However, the variation in the particle size distribution between 60 and 140 μm was negligible. The size distribution of the NAP samples was unimodal with a single peak observed at 60 μm. The width of the EAP distribution was 80 μm smaller than that of NAP. The weight mean particle diameters D_w of EAP and NAP were 142 and 213 μm, respectively. The D_w of EAP was approximately 70 μm smaller than that of NAP.

Figure 5 illustrates the XRD patterns of EAP, NAP, and commercial AP samples. The commercial AP samples had a typical XRD pattern of AP, and the XRD pattern of the NAP samples was consistent with the typical patterns of AP. Although the lattice planes of the EAP samples were similar to those of the NAP samples, the relative intensity of the (210) plane ($2\theta = 24.6$ deg) was high. This result suggested that the EAP crystals were sufficiently modified by ethylene glycol.

2. *Thermal Decomposition Behavior*

TG-DTA curves of AP were dependent on particle size. An AP sample with a D_w similar to EAP was prepared by sieving ground



a) EAP **b) NAP**

Fig. 3 SEM photographs of EAP and NAP.

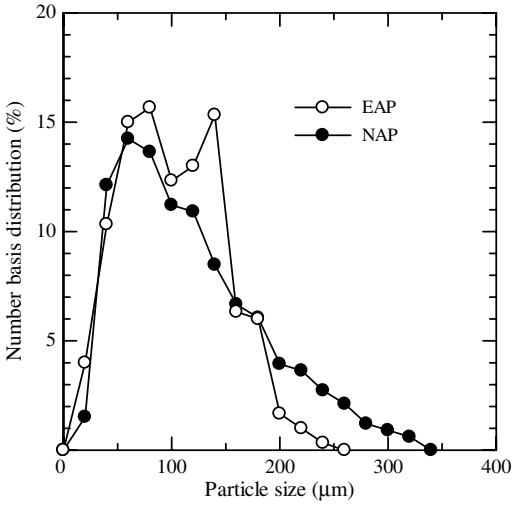
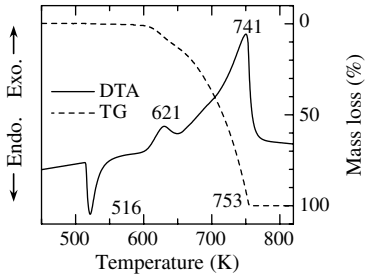
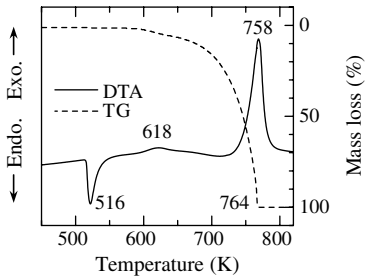


Fig. 4 Particle size distribution of EAP and NAP.



a) EAP



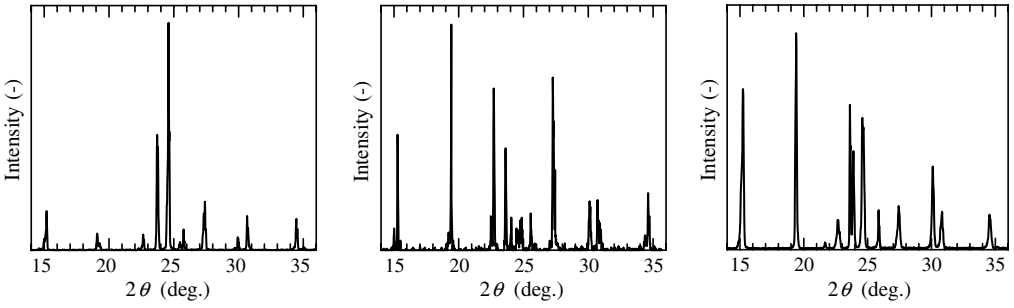
b) SNAP

Fig. 6 TG-DTA curve of EAP and SNAP.

NAP. NAP retained between 125 and 177 μm sieves yielded a D_w of 145 μm. Sample obtained by screening ground NAP was designated as SNAP.

Figure 6 shows TG-DTA curves of AP samples. In a typical DTA thermogram of AP [18–22], the endothermic peak of crystal transformation from an orthorhombic to a cubic structure was observed at 516 K. Subsequently, a low-temperature and high-temperature exothermic decomposition peak was observed around 620 K and 700–770 K. In a typical TG thermogram [18–22], a slight consumption of AP occurs at the onset of low-temperature decomposition. AP crystals exhibit Frankel defects. In such crystals, certain atoms or ions migrate to interstitial positions, which are some distance away from the holes that they vacate. These occur in AP crystals because the size of ClO^{4-} ions is much larger than that of NH^{4+} ions. The crystal defects in AP decompose during low-temperature decomposition [18,21]; however, consumption of AP at low-temperature decomposition is slight and does not affect AP consumption during high-temperature decomposition. High-temperature decomposition is the main decomposition of AP, and a rapid and complete consumption of AP occurs during this decomposition.

The DTA curve of EAP shows an exothermic decomposition peak due to low-temperature decomposition at 621 K and a remarkable exothermic decomposition peak at 741 K due to high-temperature decomposition. In the DTA curve of EAP, exothermic decomposition is observed between low-temperature and high-temperature



a) EAP **b) NAP** **c) Commercial AP**

Fig. 5 XRD patterns of EAP, NAP, and commercial AP.

decomposition. The DTA curve of SNAP shows a small exothermic decomposition peak due to low-temperature decomposition at 618 K and a remarkable exothermic decomposition peak due to high-temperature decomposition at 758 K.

From the TG curve of EAP, approximately 10% of EAP was consumed during low-temperature decomposition and approximately 90% was consumed during high-temperature decomposition. The TG curve of SNAP shows minor consumption during low-temperature decomposition. The main consumption of SNAP occurs during high-temperature decomposition and SNAP is completely consumed at 764 K. Consumption of AP during low-temperature decomposition increased with an increase in AP crystal defects [18,21]. Thus, little critical defect was present in SNAP and a critical defect of 10% was observed in EAP. As shown in Sec. III.A, the crystal habit of EAP was modified and defects in EAP were introduced by crystal modification.

The end temperature of mass loss in EAP was 753 K, which was 11 K lower than SNAP; therefore, thermal decomposition of EAP was complete at a lower temperature relative to SNAP. Thermal decomposition results revealed that EAP is an attractive oxidizer for use in composite propellants.

3. *Ignition Temperature Test*

Thermal decomposition at the surface of a propellant is more than ten thousand times higher than thermal decomposition in TG-DTA heating studies. In an ignition temperature test, a small amount of sample is introduced into a rig at a high temperature and ignition delay times are measured. This test is conducted to evaluate temperature sensitivity and kinetics of rapid heating.

From results of ignition temperature tests, activation energy of ignition can be calculated based on the relationship between temperature T (in degrees Kelvin) and ignition delay period t (in seconds) [18,22–25]. This relationship is expressed by the Arrhenius equation:

$$\ln t = E/(RT) + \text{constant} \tag{1}$$

where E is the activation energy and R is the gas constant. The value of E can be calculated from the slope of $\ln t$ versus $1/T$.

When heated to a high temperature, AP decomposes in the rig and resultant decomposition gases ignite. The decomposition and ignition of AP involves multiple steps and the reaction mechanism changes with temperature. Activation energy determined by ignition temperatures test was the total activation energy of multiple chemical reactions and physical processes that occur during ignition under rapid heating and is referred to as the apparent activation energy.

Figure 7 illustrates plots of $\ln t$ versus $1/T$ for EAP and SNAP, revealing that the slope changed at a $1/T$ of approximately 0.00135, indicating a temperature of 740 K. Results revealed that AP has two activation energies in low- and high-temperature regions, which is consistent with the results of Osada et al. [18] The flame temperature of AP is between 700 and 750 K, and the activation energy of ignition varies within this temperature range because the rate-determining step of AP ignition may change [18].

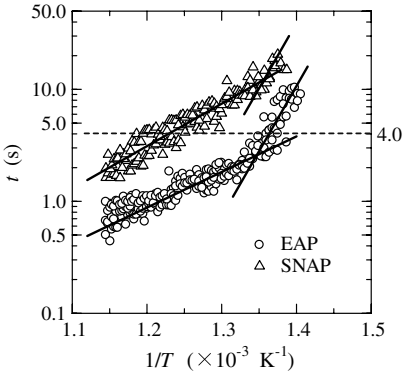


Fig. 7 Ignition temperature test of EAP and SNAP.

Table 1 E and ignition point determined by ignition temperature tests

Sample	E (kJ/mol)		Ignition point (4 s) (K)
	Low-temperature region (below 740 K)	High-temperature region (above 740 K)	
EAP	222	61	733
SNAP	223	73	811

Values of E were calculated from data in Fig. 7 and are shown in Table 1. E in the low-temperature region of EAP was almost identical to E obtained from SNAP; however, E in the high-temperature region was lower than E in SNAP. Compared with SNAP, EAP is ignited more readily at temperatures above 740 K. E in the high-temperature region is more important than E in the low-temperature region because the burning surface temperature of an AP/HTPB-based propellant with an AP content of 80% would be approximately 800 K [26,27]. Results indicated that the thermal decomposition and ignition of EAP at the burning surface of propellant would occur more readily than standard AP.

AP and binder decompose in the vicinity of the burning surface and resultant decomposition gases diffuse into the gas phase and combust. An increase in the burning rate could be achieved if AP particles decomposed more readily at the burning surface. Thus, an AP-based propellant with a high burning rate could be obtained with EAP as an oxidizer.

Explosives Society Standard-11 defines the ignition point as the temperature required to achieve ignition at 4 s [17]. Thus, the ignition point provides an indication of thermal sensitivity. Table 1 shows ignition points of EAP and SNAP. Results indicated that the ignition point of EAP is 78 K lower than SNAP, indicating high thermal sensitivity.

B. Burning-Rate Characteristics and Thermal Decomposition of Propellant

When dendritic AP was used as an oxidizer, the upper limit of AP content in the propellant was 73.5% [15]. A propellant with an AP content of 80% could be prepared with EAP due to its hexahedral crystal habit. Propellants containing EAP and SNAP were designated as propellants A and B, respectively. Figure 8 shows burning-rate characteristics of both propellants. Results indicated that burning rate increased linearly on a logarithmic scale at a pressure of 0.5–7 MPa. The burning rate (19.3 mm/s) of propellant A at 7 MPa was twice as high as the burning rate of (9.99 mm/s) of propellant B.

Propellants A and B contained AP with different size distributions. However, these distributions were monomodal and values of D_w were nearly identical for the two propellants. If crystal-habit-modified AP was not effective at enhancing the burning rate of the propellant, propellants A and B should possess similar burning rates. However, results indicated that the burning rates of propellant A were higher than those of propellant B, indicating that EAP was an

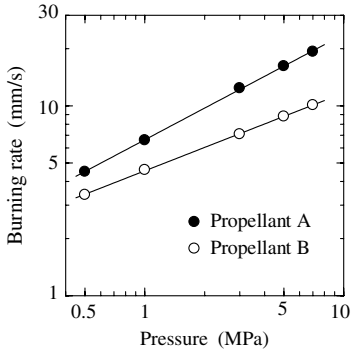
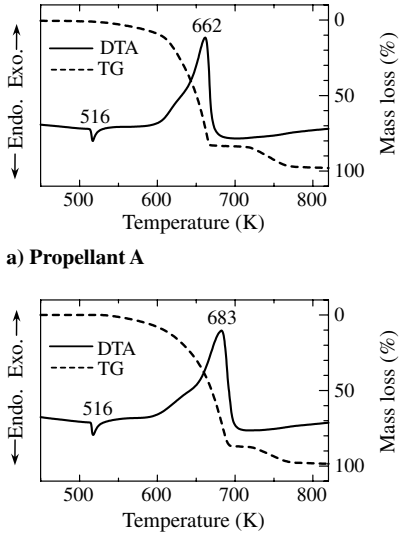


Fig. 8 Burning-rate characteristics of propellants A and B.



a) Propellant A

b) Propellant B

Fig. 9 TG-DTA curve of propellants A and B.

effective oxidizer and enhanced the burning rate of an AP-based composite propellant.

Thermochemical behavior of propellant A and B was investigated by TG-DTA. Figure 9 shows resultant TG-DTA curves of both propellants. In the DTA curve of propellant A, an endothermic peak was observed at 516 K due to crystal transformation of AP and an exothermic peak at 662 K due to decomposition. In the TG curve, the majority of consumption occurred between 600 and 670 K due to exothermic decomposition and a minor amount of consumption was observed between 720 and 760 K. HTPB decomposed between 600 and 760 K and a remarkable consumption was observed between 700 and 760 K [28]. The small mass loss observed in propellant A was due to the consumption of residual HTPB during propellant decomposition.

In the TG-DTA curve of propellant B, decomposition occurred between 600 and 700 K, and an exothermic peak was observed at 683 K. Peak temperature and end temperature of propellant A decomposition was approximately 20 K lower than propellant B. As described in Sec. III.A.2, the peak due to high-temperature decomposition of EAP is significantly lower than SNAP, which causes a decrease in the decomposition temperature of propellant A. The exothermic decomposition peak of AP-based propellant is shifted to lower values by the addition of Fe_2O_3, a burning catalyst

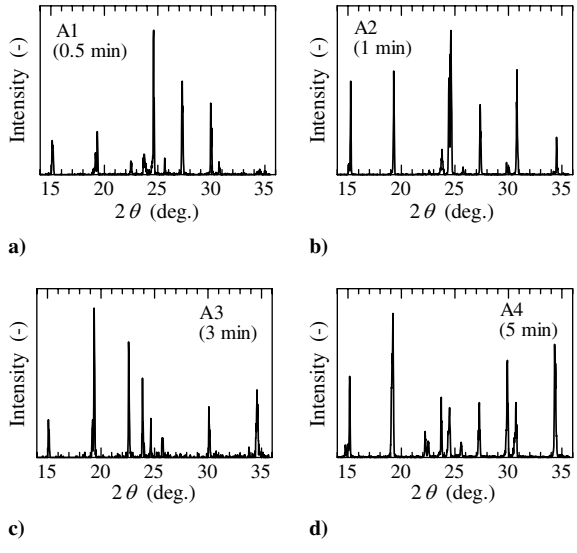


Fig. 10 XRD pattern of samples A, B, C and D.

Table 2 Variation of D_w and ξ with grinding time

Symbol	EAP	A1	A2	A3	A4	NAP
Grinding time (min.)	0	0.5	1	3	5	0
D_w (μm)	142	103	84	62	47	213
ξ (-)	0.43	0.33	0.27	0.07	0.06	0.04

[29–31]. Although Fe_2O_3 were not incorporated into propellant A, similar thermal decomposition behavior was obtained with the use of EAP as an oxidizer.

C. Influence of Crystal Habit Modification on Burning Rate

It was hypothesized that the crystal habit of EAP would be lost by grinding and the magnitude of modification would decrease with an increase in grinding time. Thus, the effect of grinding time on the extent of EAP modification was investigated. EAP was ground by a vibration ball mill for 0.5, 1, 3, and 5 min. Ground EAP samples were observed by SEM and the D_w of each sample was measured. Table 2 displays values of D_w for ground EAP. Results indicated that D_w decreased with an increase in grinding time.

Figure 10 shows XRD patterns of ground EAP samples, A1–A4. Planes of A1–A4 agree with those of EAP; however, samples produced XRD patterns with varying intensity. As grinding time increased, XRD patterns became more similar to those of NAP. As a result, XRD patterns of A3 and A4 were almost identical to those of NAP.

According to the ASTM of AP, peaks appear at 15.3, 19.4, 22.7, 23.9, 24.6, 27.4, 30.1, 30.8, and 34.6 deg of 2θ. As described in Sec. III.A.1, the relative intensity of the (210) plane ($2\theta = 24.6$ deg) of EAP was remarkably high. The ratio of lattice plane intensity (210) to the total intensity of each peak, ξ indicates the extent of crystal habit modification [16] and was calculated from XRD patterns of each sample. Results in Table 2 revealed that ξ decreased with an increase in grinding time, until a grinding time of 3 min was reached. A grinding time of 3 min led to a ξ (A3 and A4) that was nearly identical to NAP. These results suggested that the magnitude of crystal habit modification in EAP decreased with an increase in grinding time and disappeared with a grinding time of more than 3 min.

AP samples with a D_w nearly identical to those of A1–A4, were prepared by sieving ground NAP. Table 3 shows the screen size of sieves and D_w of AP samples. The D_w of B1–B4 are almost identical to those of A1–A4, respectively. As shown in Tables 2 and 3, propellants were prepared with AP samples B1–B4 and the burning rates were investigated. Figure 11 shows the burning-rate characteristics of propellants using samples A1–A4 and B1–B4. Data in Fig. 11 revealed that burning rates of propellants prepared from A1 and A2 were higher than those of propellants incorporating B1 and B2. However, the burning rates of propellants prepared with A3 and A4 were almost identical to propellants containing B3 and B4, respectively.

The ratio of propellant burning rate incorporating ground EAP to the burning rate of propellant with NAP, $B_r(-)$, was calculated from data in Figs. 8 and 11. Figure 12 shows the effect of ξ on B_r at 1 and 7 MPa. The value of B_r was equal to one with a ξ less than 0.15. Because of the low magnitude of crystal habit modification in these propellants, burning-rate characteristics were not affected. However, propellants with a ξ greater than 0.15 showed a significant increase in

Table 3 D_w of AP samples prepared by sieving ground NAP

Symbol	Opening of sieve (μm)		D_w (μm)
	Upper	Bottom	
B1	105	90	95
B2	90	75	81
B3	63	53	57
B4	53	44	41

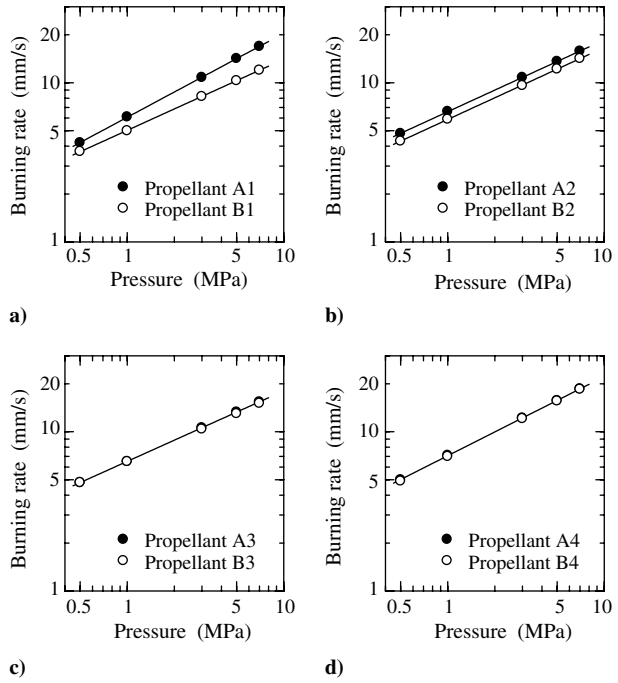


Fig. 11 Burning-rate characteristics of propellants using samples A1–A4 and B1–B4.

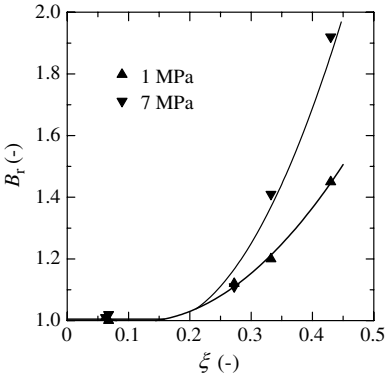


Fig. 12 Effect of ξ on B_r at 1 and 7 MPa.

B_r due to an increase in ξ. Furthermore at 7 MPa, a larger increase in B_r was observed than at 1 MPa. Thus, with values of ξ greater than 0.15, crystal habit modification had an effect on the burning rate.

IV. Conclusions

Hexahedral crystal-habit-modified AP was prepared with ethylene glycol, resulting in a mean particle diameter of 142 μm. Mass loss associated with low-temperature decomposition of modified AP was approximately 10% and the peak temperature of high-temperature decomposition shifted to lower temperatures compared with typical AP. Above 740 K, the activation energy for ignition of modified AP was lower than standard AP. Thermal decomposition and ignition behavior of modified AP were more likely to enhance the burning rate, compared with standard AP.

Compared with propellant using dendritic-modified AP, propellant with a higher AP content was prepared using hexahedral-modified AP. Additionally, the burning rate of propellant incorporating hexahedral-modified AP was higher than propellant with standard AP. Thus, hexahedral crystal-habit-modified AP prepared with ethylene glycol was an effective oxidizer that enhanced the burning rate of AP-based composite propellant. The effect of crystal habit modification on burning rate was dependent on the magnitude of modification.

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