Combustion characteristics of ADN-based solid propellants

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ABSTRACT

Ammonium perchrolate (AP) is the most useful oxidizer for the solid rocket motors (SRMs) under the present situation, however it is also the source of the environmental pollution close to the launch site. It is well known that HCl is exhausted through the firing of SRMs and its concentration reaches approximately 10 to 20 mole percent of the total exhaust. 'Environmentally friendly' and 'High performance' are required for the next-generation SRMs. In this study, ammonium dinitramide (ADN), which has recently attracted attentions as a halogen-free oxidizer was employed for a substitution of AP and the combustion properties of the composite propellants were investigated. Thermoplastic elastomer (TP) and hydroxyl-terminated butadiene polymer (HTPB) were used as a binder for this research. Pyrotechnic sensitivity analysis was conducted to estimate the safety of TP/ADN propellants. Strand burning tests were also carried out for all samples and the burning rate and temperature profile were obtained through these experiments. It was found that the burning rate characteristics of ADN-based propellants were influenced by the binders.

1. INTRODUCTIONS

The conventional AP based composite propellants have been widely used for a long time, however from an environmental perspective, HCl exhausts have been recently concerned, and the development of environmentally friendly propellants should be encouraged in addition to improvements of the specific impulse.

The ways for the reduction of the HCl mass ratio in exhaust gases have been reported. Scavengers, neutralized and nitramine method have been proposed. However, it is difficult to get rid of HCl completely from the exhausted gases by these ways, and moreover they lower the specific impulse.

Nowadays ammonium nitrate (AN), cyclo-tetra-methylene tetra-nitramine (HMX), hexanitrohexaazaisowurtzitane (CL-20), ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF) are main candidates of the halogen-free material for the solid propellants. Figure1 shows the properties of these substances with two indices. There are no materials having high values for both indices at present. HMX and CL-20 have high heat of formation and have been studied about the thermal decomposition and the burning properties. However, both substances are ineffective as the oxidizer due to the negative oxygen balance. On the other hand, AN, ADN and HNF have positive oxygen balances

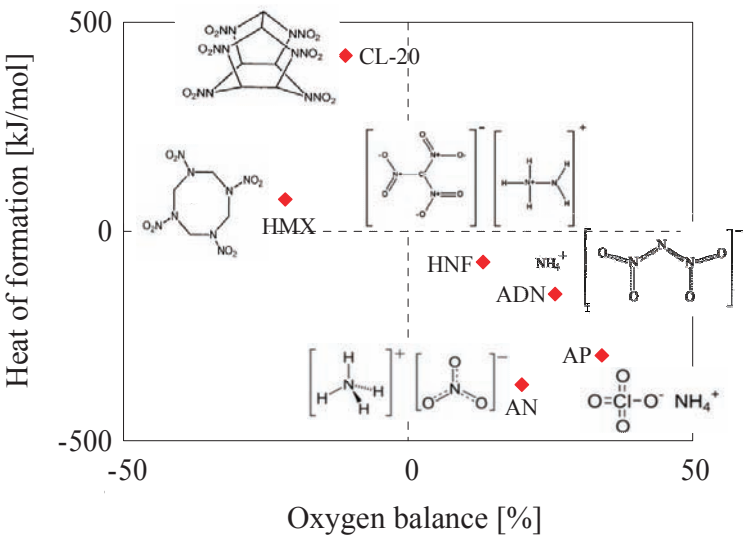


Fig. 1 Properties of oxydizers

and they are effective for the propellant performance.

The theoretical specific impulses (Isp) of the propellants containing these halogen-free materials were shown in Figure 2. The mass ratio of hydroxyterminated poly-butadiene polymer (HTPB): aluminium (Al) was fixed at 3:4 and the oxidizer to fuel ratio was changed. HMX-based propellant has the low peak of the Isp value. ADN and HNF composite propellants show higher Isp value than AP.

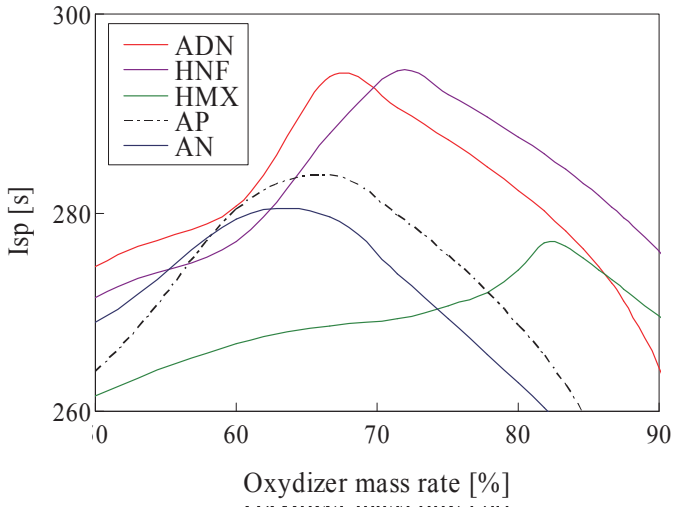


Fig. 2 Dependence of Isp on oxydizer mass rate

The availability and the cost of these materials should be considered for rocket motor applications. The way of ADN synthesis has been recently improved. The safe and simple method has been developed. In HNF synthesis, some explosive and toxic substances have to been treated and therefore it is thought that the mass production of HNF is more difficult than ADN.

From above reasons, we have decided that ADN is the most promising material as a substitution of AP. In this report, ADN studies were shortly reviewed and combustion characteristics of ADN based composite propellants were discussed.

2. ADN STUDIES

In 1970s ADN was synthesized at Russia for the first time and in 1980s' it was also reported by Bottaro et al[1] in the U.S. By the mid 1990s, these synthesis methods were developed independently and became similar and now they are known as 'Urethane method'[2]. At the same time breakthrough was done by Langlet et al in Sweden[3]. The method requires only one nitration process, and the nitration reagent is low-cost.

Crystalization processes of ADN were also developed after the establishments of the synthesis method. ADN crystals just synthesized are needle shape, therefore ADN crystals have to be processed to spherical shape. Prilling and recrystalization are well known for the process. There are two ways for prilling methods, and one of them is recrystalization in specific solvent[5] and the other is spray melted ADN in a spray tower[6]. Recrysallization enables to lower the aspect ratio of crystals, and it have been reported that some salts of calcium are especially effective additives[7]. ADN is so hygroscopic that it should be coated with hydrophobic thin layer after the crystallization process. For example, silica layer coating[6] in spray tower and coating method in super fluid turbulence[8] are proposed. Standard method of these processes has not been established yet due to the low melting points and highly hygroscopic nature.

An appropriate binder selection is a very important step for the developments of ADN-based solid propellants. Binders must have adequate mechanical properties and not react with the other ingradients. HTPB, which is a common binder for SRMs, shows a little reactivity with ADN, so it can not be applied without improvements[9]. In case glycidyl azide polymer (GAP), which is one of the high energy materials, was applied as a binder, the propellant can be cured by addition of N-methyl-p nitroanilin as a stabilizer [10]. The adhesion between binder and ADN particles has not been reported, so the evaluation will be future studies.

Combustion characteristics of ADN pellets and ADN-based propellants have been widely investigated. As the binder, paraffin[11], polybutadiene acrylic acid acrylonitrile (PBAN)[12], HTPB[13], poly-Caprolactone[14] and GAP [10] were studied and the burning rates and surface temperatures were reported. According to these reports, the burning rates and the pressure exponents tend to be higher than those of AP-based propellants. For example, improving the binders and addition of burning rate catalysts[14] have been tried to decrease the pressure exponent.

Understanding the combustion mechanisms by numerical modelings have been also reported [15], but experimental burning rates have not been accurately simulated. This is caused by inaccurate elementally reaction model and the bubbles or droplets model in the condensed phase. It is difficult to simulate the real

phenomenon because ADN melts at low temperature and blown off from the burning surface as liquid droplets[16].

Small rocket motor tests have been reported by only one group[17] because the manufacture of grains with good mechanical properties and low pressure exponent is still difficult. For example, the group reported that GAP is compatible with ADN, but the other reported that GAP and isocyanates mixture generates a soft form[10] without any improvements. Many tasks shown in above must be solved and reliable methods are necessity for an environmentally friendly and high performance propellant.

3. EXPERIMENTAL

3.1 Sample Preparation

ADN used in this study was prepared in house. The needle-shape ADN crystals had a melting point 360–363K. UV-spectroscopic analysis indicated approximately 95% purity and the impurity was identified as ammonium nitrate by the TG-DTA thermal analysis. TP and HTPB were employed as the binder in this report. Rubber-like and low-melting TP shown in Fig. 3 was supplied for this study by Katazen Co., Ltd. It was specially prepared to show the lower melting point than ADN and the melting temperature was 343K. In the case that HTPB was applied as the binder, needle-shape ADN crystals must be prilled to suppress the viscosity of the slurry. Coarse and fine prilled ADN were prepared by the emulsion method[9] with non-polar solvents and they are shown in Fig.4(a) and 4(b) respectively. The mean volume diameter of the course particles was 300μm and that of fine particles was 99μm. The mixture ratio of the coarse and fine particles was determined to show the lowest viscosity and it was fixed at 3:1.

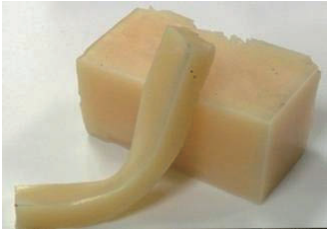


Fig. 3
Thermoplastic polymer (TP)

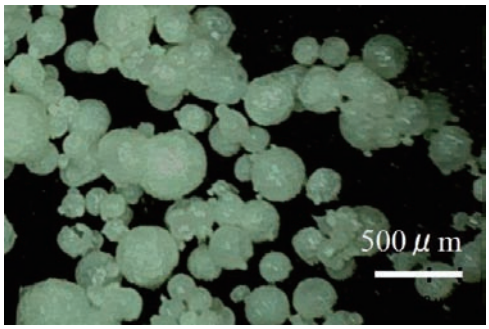


Fig. 4(a)　Coarse prilled ADN

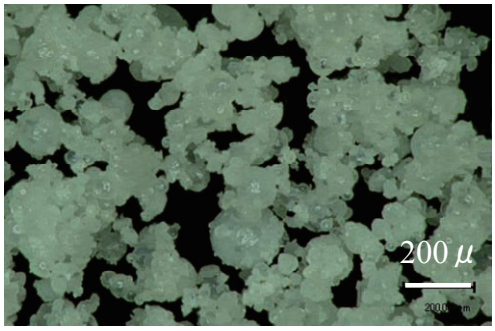
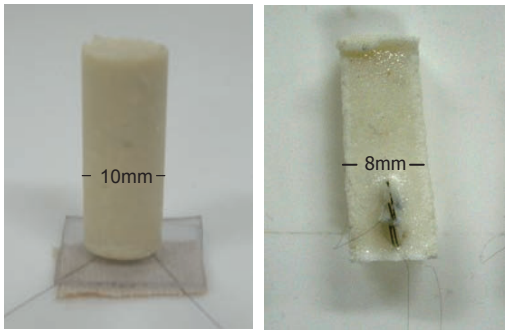


Fig. 4(b)　Fine prilled ADN

TP/ADN samples have been prepared by the following procedures, needle–shape ADN crystals were well mixed with the melted TP at 343K and the mixture was casted and pressed in a mould. The strand sample which is shown in Fig.5(a) was solidified after cool down to the room temperature. No reactions were observed while the propellant was stored at room condition for a month.

HTPB pre-polymer and the prilled ADN were mixed well. The mixture was deformed and cured at room temperature because change in color was observed at 330K. 'PB/ADN' sample shown in Fig.5 (b) was prepared.

Table 1 shows the composition of samples for this study.



(a) 'TP/ADN-2'　(b) 'PB/ADN'
Fig.5　Propellant samples

Table 1. Composition of each sample

Sample	Fuel (Binder)	Oxydizer	Fuel:Oxydizer (mass%)
TP/ADN-1	TP	ADN	30:70
TP/ADN-2	TP	ADN	20:80
TP/ADN-3	TP	ADN	10:90
TP/AP	TP	AP	20:80
PB/ADN	HTPB	ADN (prill)	30:70

3.2 Pyrotechnic Sensitivity Test

Drop hammer, friction and electrostatic sensitivity of fine ADN crystals and 'TP/ADN-2' were evaluated. They are standardized in 'JIS K 4810'. The drop hammer impact sensitivity was evaluated by the limiting height at which an explosion was obtained at least one out of 6 trials (1/6 explosive point). In this study, a 5kg hammer was set. The friction sensitivity test corresponds to the BAM sensitivity one. In the electrostatic sensitivity test, up to 10 J was discharged.

3.3 Strand Burning Test

Burning rate was measured in a strand burner purged with nitrogen. TP/ADN and TP/AP strands, 10mm in diameter and over 25mm in length, were employed. PB/ADN strands were square pole shape; 8mm in width and over 20mm in height.

Thermocouples are inserted from the bottom of the mould like Fig.6 before the slurry is casted. W/Re(5%) –W/Re(25%) thermocouples whose diameter was 100μm were used for the flame temperature measurements of the TP/ADN and TP/AP samples. The final flame temperature of TP/ADN strand reached over the measurable limit of Pt-Pt/ Rh(13%) type, therefore W/Re(5%) –W/Re(25%) thermocouples were employed. For HTPB/ADN samples, Pt–Pt/Rh(13%), ϕ=25μm thermocouples were used.

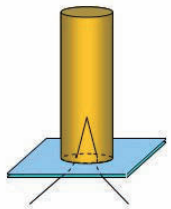


Fig. 6 Embedded thermo-couple image

4. RESULTS and DISCUSSION

4.1 Pyrotechnic Sensitivity Analysis

The drop hammer impact, friction and electrostatic sensitivity data for the fine ADN crystals and 'TP/ADN-2' are summarized in Table 2. According to the drop hammer sensitivity test, the crystals and 'TP/ADN-2' were sensitive to drop hammer impact since the height of '1/6 explosive point' was 5–10cm and 15–20cm respectively. Both of the crystals and the propellant samples have ignition forces greater than 353N, and the electrostatic ignition energies greater than 10J. Therefore, their friction and electrostatic sensitivities are not high. From these results, it was indicated that fine ADN crystals and the ADN-based propellant are required to be handled with care, particularly for drop hammer impacts.

Table 2 Pyrotechnic Sensitivity Results

	fine ADN crystal	'TP/ADN-2'
Drop Hammer Impact (cm)	5–10	15–20
Friction (N)	＞353	＞353
Electrostatic (J)	＞10	＞10

4.2 Burning Rate Characteristics

The flames of ‘TP/ADN’ and ‘TP/AP’ samples at approximately 5MPa were shown in Fig.7. All samples burned continuously with steady flames and melting layers. It is considered that the melting layers were caused by TP because conventional AP propellant does not form a melting layer. It was also observed that the droplets are blown off from the combustion surface.

‘TP/AP’　‘TP/ADN-1’　‘TP/ADN-2’　‘TP/ADN-3’

Fig. 7　The Flame of ‘TP/AP’ and ‘TP/ADN’ samples

The linear burning rates were plotted in Fig.8. The pressure exponents of ‘TP/ADN-1, 2, 3’ and ‘TP/AP’ were 2.7, 1.0, 0.7 and 0.3 respectively. It has been reported that a pure ADN shows an plateau burning at the pressure range of 2-10MPa and the pressure exponent is very low (0.1-0.2)[18]. Therefore, it considered that the ADN mass ratio contributed to decreasing the value.

Figure 9 shows the flames of ‘PB/ADN’ at 2, 5 and 8MPa. At 2MPa, smoldering and unstable combustion involving the thick melting layer was observed. At 5 and 8MPa, stable combustion was kept and the melting layer was thicker at 5MPa than 8MPa.

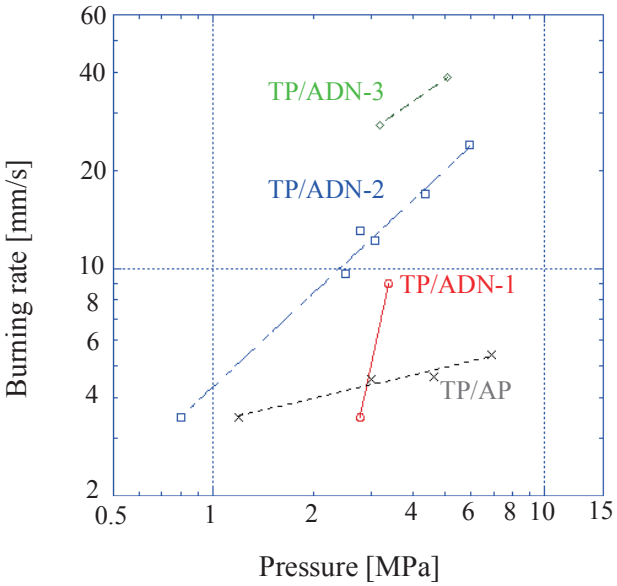


Fig. 8　Linear burning rates of‘TP/AP’ and ‘TP/ADN’ samples

2MPa　5MPa　8MPa

Fig. 9　The Flames of ‘PB/ADN’ samples

The linear burning rate of 'PB/ADN' was plotted in Fig.10. 'TP/ADN-1', which has the same O/F value, was also plotted for the comparison. The burning rate of 'PB/ADN' is as high as that of 'TP/ADN-1' at approximately 3MPa. The pressure exponent is 1.1 and it is lower than that of 'TP/ADN-1'. The difference of thermal properties of binders affects the burning rates and pressure exponents. The melting layer may influence to the burning properties of ADN-based propellants.

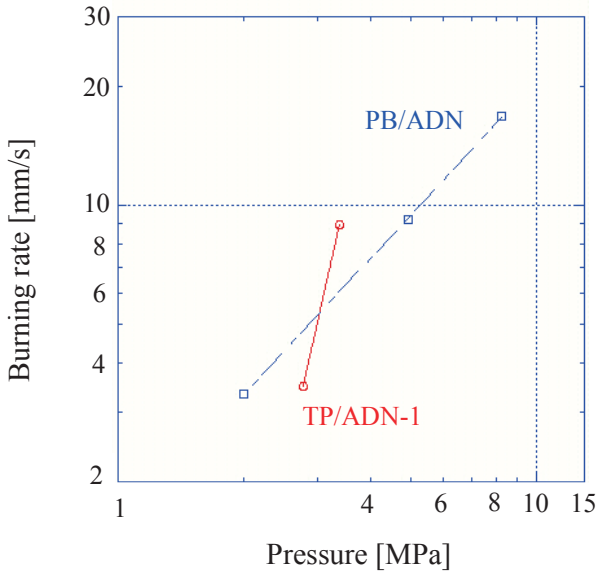


Fig. 10 Linear burning rate of 'PB/ADN' and 'TP/ADN-1'

4.3 Flame Temperature

The flame temperature profiles of TP/AP, TP/ADN, and ADN/HTPB samples are shown in Figs. 11, 12 and 13. The burning surface was assumed as the inflection point. At each test, the final flame temperature reaches near the adiabatic one which is shown by horizontal dashed line. Relatively large discrepancy between the flame temperature and the theoretical one is probably caused by the inaccuracy of the formation heat of TP. As for 'TP/ADN-3', the measured value was limited by the measurement limit temperature (2600K) of the thermocouple.

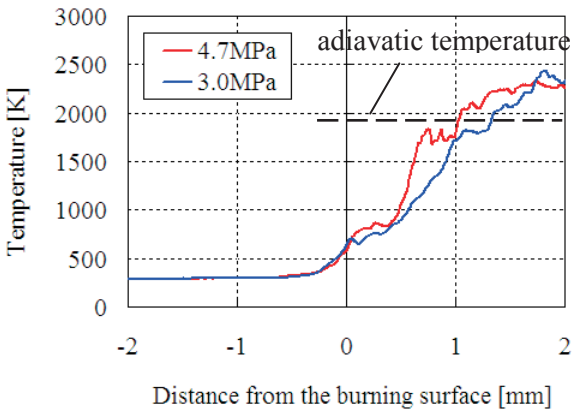


Fig. 11 Flame temperature of 'TP/AP'

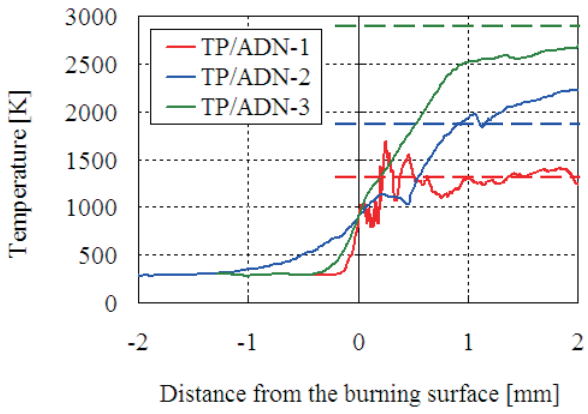


Fig 12 Flame temperature of 'TP/ADN'

5. SUMMERY

Combustion characteristics of the ADN-based propellants were investigated. Thermoplastic polymer (TP) and HTPB were employed as the binder. Pyrotechnic sensitivity test was carried out and it was found that ADN should be handled with care particularly for drop impacts. The linear burning rate and the flame temperature were measured for TP/AP, TP/ADN and TP/ADN samples. The linear burning rates of TP/ADN samples were several times faster than that of TP/AP ones. ADN-based sample showed the high pressure exponent for SRMs use and the value was suppressed with increasing the mass ratio of ADN in the case of TP binder. The pressure

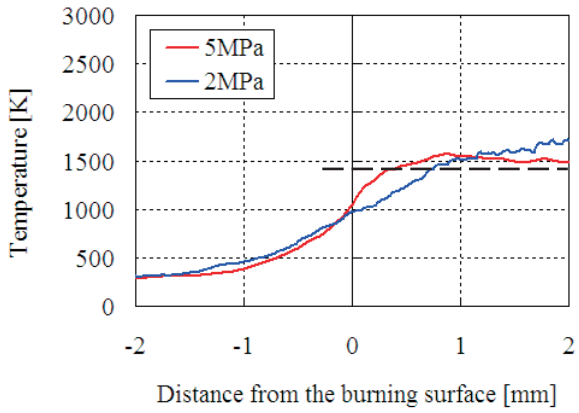


Fig. 13 Flame temperature of 'PB/ADN'

exponent of ADN/HTPB propellant was lower than that of TP/ADN. The final flame temperature achieved to near the theoretical value in each sample. Further combustion work by more accurate way is needed to understand the burning surface behavior. From this investigation, it was found that the thermal properties of binder affect their combustion characteristics, so more appropriate ADN-based propellants may be developed by improving the binders.

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