研究論文

Combustion mechanism of high energy composite propellants (V)

— Combustion of azide/nitramine propellants —

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The combustion wave structure was examined by using fine thermocouples in order to elucidate the control process of burning rate of azide/nitramine propellants. From the experiments, it was found that the burning rate of AMMO(3-azidemethyl-3'-methyloxetane)/EDNA(ethylenedinitramine) propellant was higher than that of AMMO/HMX(cyclotetramethylenetetranitramine) propellant and the pressure exponent of AMMO/EDNA propellant was lower than that of AMMO/HMX propellant. The temperature profile in the combustion waves of the propellants revealed that there was a large heat release at the burning surface. This exothermic decomposition reaction at the burning surface is found to be mainly responsible for the burning rate of AMMO/EDNA and AMMO/HMX propellants. It is explained by the larger heat release of AMMO/EDNA propellant at the burning surface that AMMO/EDNA propellant has the higher burning rate than AMMO/HMX propellant.

Introduction

Theoretical and experimental studies have been conducted on the combustion of azide polymers used as a binder in high-energy propellants[1~4]. AMMO(3-azidemethyl-3'-methyloxetane) is one of the energetic azide polymers which contain N_3 groups in their molecular structures[2]. Since the concentration of oxygen atom contained within AMMO is low, the heat released by the combustion is not due to the oxidation reaction, but due to the scission of the $-N_3$ bond to form N_2 gas. Furthermore, the combustion potential of AMMO could be increased by the addition of oxidizers such as ammonium perchlorate(AP), ammonium nitrate(AN), and nitramines. The energetic propellants composed of the oxidizers and AMMO as an energetic binder are considered to be used as high-energy propellants.

A great deal of attention has been focused on the combustion mechanisms of inert hydrocarbon binder/nitramine propellants. This is because nitramine propellant produce relatively high specific impulses, even though the adiabatic flame temperature is low[5,6]. Furthermore, the combustion products are not only smokeless but also noncorrosive. Thus, there have been a number of experimental and theoretical studies on the combustion of nitramines and inert binder/nitramine propellants[7~11]. The burning rate of the inert hydrocarbon binder/HMX is very low because of the endothermic decomposition of the binder[7]. EDNA(ethylenedinitramine) is a linear nitramine which has modest properties in the flame temperature and the molecular weight of burned gases as compared with HMX(cyclotetramethylenetetranitramine) and NQ(nitroguanidine). The burning rate of double base propellants is increased and the pressure exponent is decreased by the addition of EDNA[12].

In the present study, AMMO/EDNA propellant was formulated and the burning rate characteristics and combustion wave structure were investigated in order to gain a wide spectrum of burning rate.

Experimental

AMMO used in the present study was produced by replacing C-OH bond of 3-methyl 3-oxetane methanol with $C-N_3$ bond. AMMO without curing and crosslinking was slightly yellowish viscous liquid. The terminal OH groups of AMMO were cured with the NCO groups of IPDI (isophorone diisocyanate). Finely crystallized nitramines

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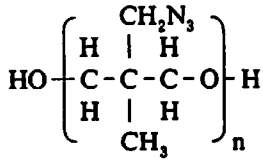
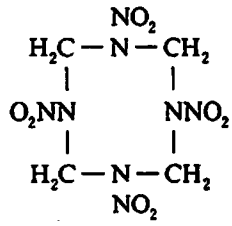
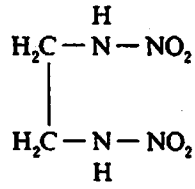
Table 1 Physical and chemical properties of energetic materials

Name	AMMO	HMX	EDNA
Structural Formula			
Gross formula	$C_5H_9ON_3$	$C_4H_8N_8O_8$	$C_2H_8N_4O_4$
Mg (kg/kmol)	5100	296.2	150.1
ΔH_f (kJ/kg)	+345.3	+252.7	−688.7
ρ (kg/m^3)	1.06×10^3	1.96×10^3	1.71×10^3
T_f (K)	1283	3300	2628

Mg: Molecular mass, ΔH_f: Heat of formation, ρ: Density,
T_f: Adiabatic flame temperature.

Table 2 Chemical composition of propellants used in this study

Propellants	Weight fraction (%)		
	AMMO	EDNA	HMX
AMMO/EDNA	25	75	
AMMO/HMX	25		75

EDNA and HMX were used in this study. The chemical structure and properties of the energetic materials are shown in Table 1. The formulation of the propellants is shown in Table 2.

The theoretical rocket performance of the propellants which are composed of oxidizer and AMMO is calculated by using NASA SP-273 based on JANNAF Thermochemical Table.

The experimental investigation of burning rates and combustion waves was conducted using a chimney type strand burner which was pressurized with nitrogen gas. The burning process was recorded with a high-speed video camera through a transparent window attached to the side of the burner. The temperature profiles in the combustion wave structure were measured with microthermocouples (5μm in diameter Pt-Pt-10%Rh wire) being embedded in the samples.

Results and discussion

Theoretical rocket performance of AMMO/EDNA and AMMO/HMX propellants

The theoretical rocket performance of AMMO/EDNA and AMMO/HMX propellants are shown in Fig. 1. The

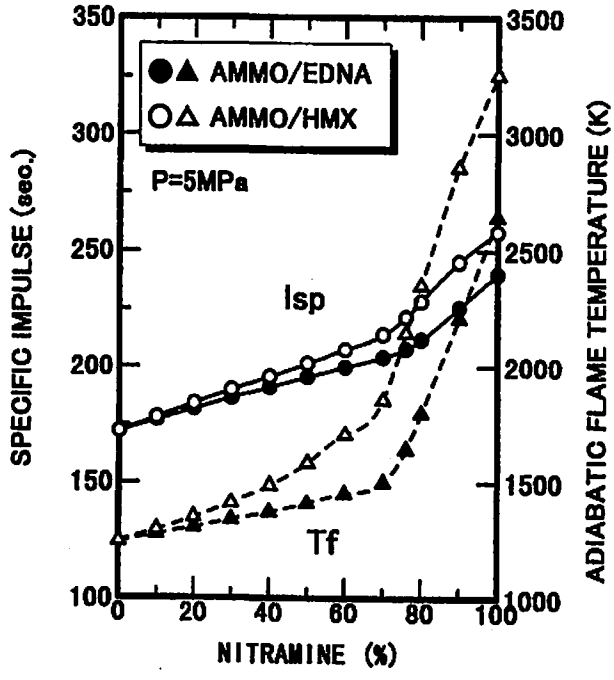


Fig. 1 Theoretical combustion performance of AMMO/EDNA and AMMO/HMX propellants

specific impulse (Isp) and adiabatic flame temperature (T_f) of both propellants are increased by the addition of nitramine. Isp and T_f are increased drastically over 70% of nitramine content. Both Isp and T_f of AMMO/HMX propellant are larger than those of AMMO/EDNA propellant.

Burning rate characteristics of AMMO/EDNA and AMMO/HMX propellants

The burning rates of AMMO/EDNA and AMMO/HMX propellants showed approximately straight lines in a ln r vs. ln P plot as shown in Fig. 2. The pressure expo-

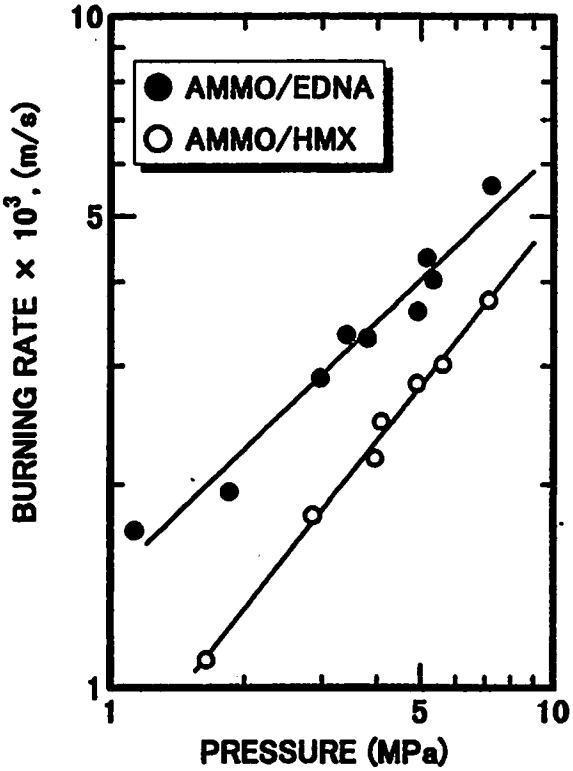


Fig. 2 Burning rate characteristics of AMMO/EDNA and AMMO/HMX propellants

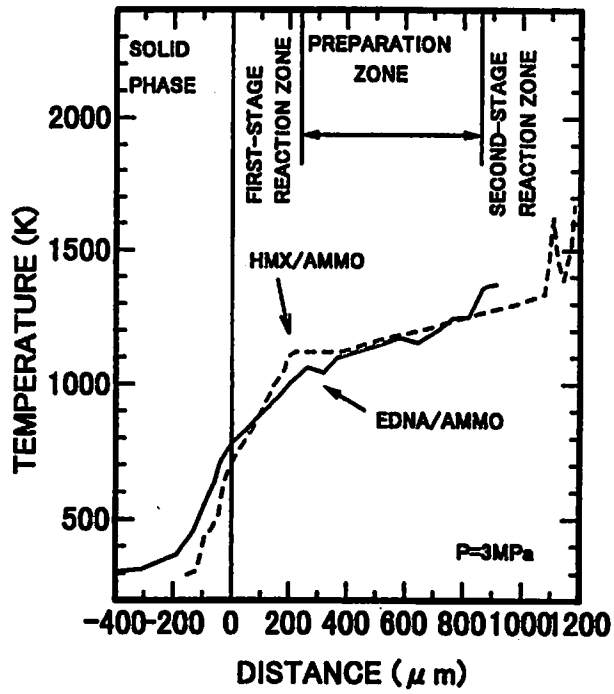


Fig. 3 Temperature profiles in the combustion waves of AMMO/EDNA and AMMO/HMX propellants

nent of the burning rate at a constant initial temperature is denoted by the following equation:

$$n=(\partial \ln r/\partial \ln P)_{T0} \quad (1)$$

It was 0. 61 for AMMO/EDNA and 0. 80 for AMMO/HMX propellants. The burning rate of AMMO/EDNA propellant is higher than that of AMMO/HMX propellant and the pressure exponent of AMMO/EDNA propellant is lower than that of AMMO/HMX propellant.

Combustion wave structure

The combustion process of both AMMO/EDNA and AMMO/HMX propellants was studied using temperature profiles measured in the combustion waves. As shown in Fig. 3, the measured temperature profiles show a steep temperature gradient near the burning surface, i.e., the first-stage reaction zone. The steep temperature gradient flattens out some distance from the surface, i.e., preparation zone. The second steep temperature gradient occurs at the boundary between the preparation zone and luminous flame zone, i.e., the second-stage reaction zone. The combustion wave structure of AMMO/EDNA and AMMO/HMX propellants was found to be very similar to that of inert polymer/HMX propellants[7,8].

In order to understand the combustion process of azide/nitramine propellants, the burning surface temperature (T_s) and temperature at the end of the first-stage reaction zone (T_g) for AMMO/EDNA and AMMO/HMX propellants were measured. As shown in Fig. 4, T_s and T_g increase with increasing pressure for both AMMO/EDNA and AMMO/HMX propellants. T_s and T_g for AMMO/EDNA and AMMO/HMX propellants are approximately the same in the pressure range between 1. 0 and 5. 0 MPa.

The temperature gradient, $(dT/dx)_{s,g}$, at the burning surface was measured to determine the heat transfer from the gas phase to the burning surface. Though the temperature gradient in the first stage reaction zone are scattered in Fig. 5, it is evident that $(dT/dx)_{s,g}$ increases with increasing pressure for both AMMO/EDNA and AMMO/HMX propellants. While the burning rates differ in the two propellants, the reaction rate in the gas phase just above the burning surface, which is characterized by $(dT/dx)_{s,g}$, was the same for both propellants.

To determine the heat of reaction at the burning surface (Q_s), an energy balance at the burning surface was used. This energy balance equation is represented by the following equation:

$$\rho_p C_p r (T_s - T_0) = \lambda_g (dT/dx)_{s,g} + \rho_p r Q_s \quad (2)$$

where ρ_p = density of propellant (kg/m³), C_p = specific heat of propellant (kJ/kgK), r = burning rate (m/s), T_0 = initial temperature (K), and λ_g = heat conductivity (kJ/smK). The results of the computation are shown in Fig.

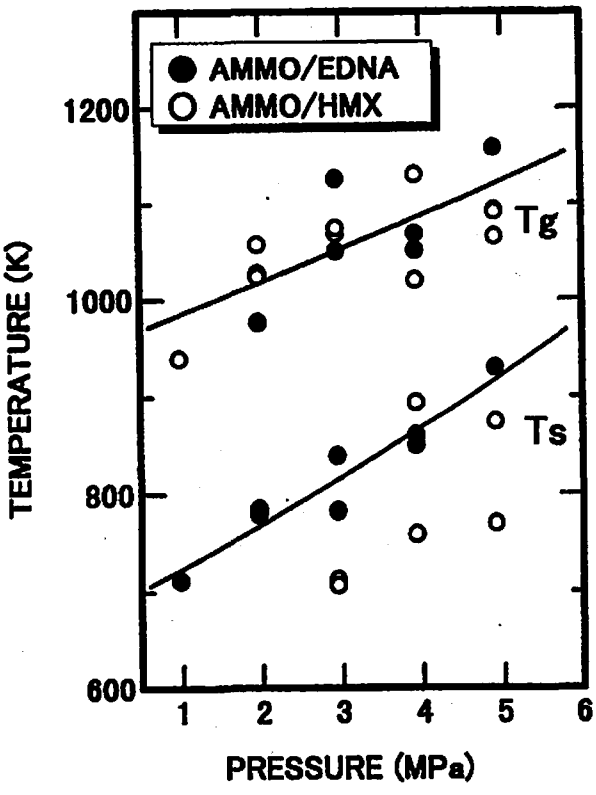


Fig. 4 Burning surface temperature(T_s) and temperature at the end of the first-stage reaction zone(T_g) vs. pressure for AMMO/EDNA and AMMO/HMX propellants

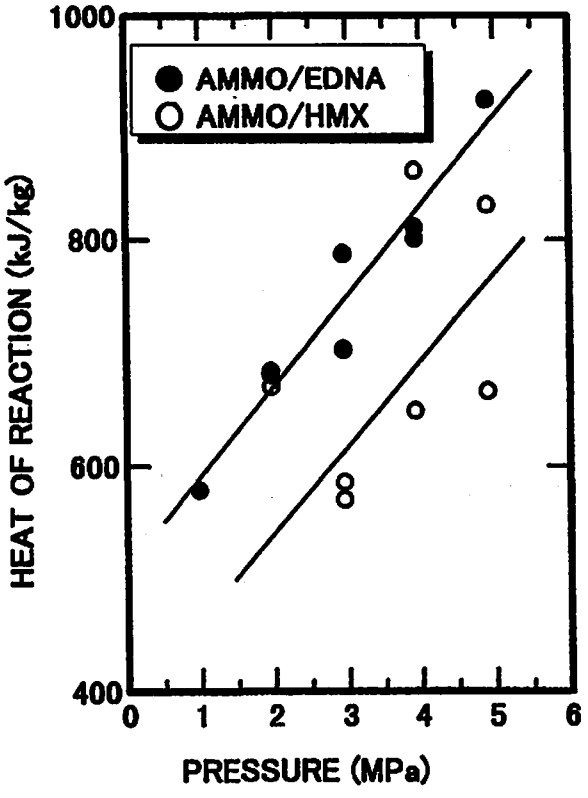


Fig. 6 The heat of reaction at the burning surface of AMMO/EDNA and AMMO/HMX propellants

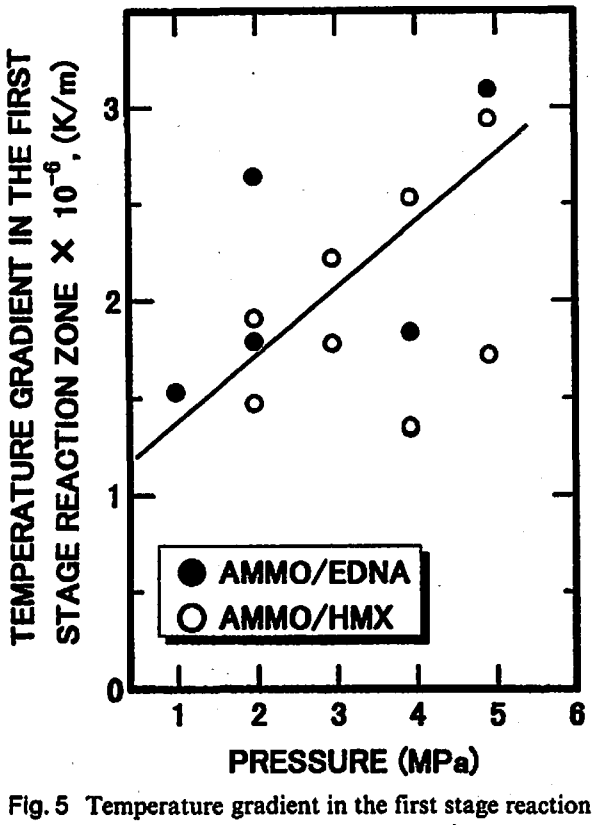


Fig. 5 Temperature gradient in the first stage reaction zone vs. pressure for AMMO/EDNA and AMMO/HMX propellants

6. The scatter in the data is high because of the scatter in the $(dT/dx)_{s,g}$ used in the computation. Nevertheless, the difference between AMMO/EDNA and AMMO/HMX propellants can be seen in Fig. 6. The heat of reaction at the burning surface for AMMO/EDNA propellant is larger than for AMMO/HMX propellant.

The heat flux transferred back from the gas phase to the burning surface ($\lambda_g(dT/dx)_{s,g}$) and the heat released at the burning surface ($\rho_p r Q_s$) were calculated. The results are shown in Fig. 7. In computation, the heat conductivity, λ_g was assumed to be 5.02×10^{-3} kJ/smK. It can be seen that the heat flux for both AMMO/EDNA and AMMO/HMX propellants is approximately the same and is relatively pressure insensitive.

As shown in Fig. 7, the heat released at the burning surface increases with increasing pressure. The heat released at the burning surface for AMMO/EDNA propellant is larger than that for AMMO/HMX propellant in the range of the pressure between 1. 0 and 5. 0 MPa. When the heat flux transferred back from gas phase to the condensed phase was compared with the heat flux released at the burning surface, the former was much less than the latter for AMMO/EDNA and AMMO/HMX propellants. The ratio of the former to the latter is estimated to be 0. 02 for

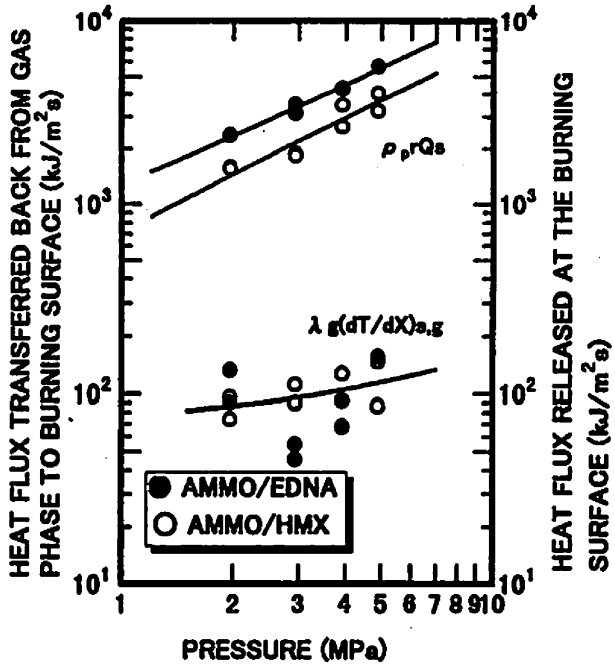


Fig. 7 Heat flux transferred back from gas phase to burning surface and heat flux released at burning surface for AMMO/EDNA and AMMO/HMX propellants

AMMO/EDNA propellant and 0. 03 for AMMO/HMX propellant at 4. 0 MPa. The results indicate that the exothermic reaction at the burning surface is supposed to be mainly responsible for the burning rate of azide/nitramine propellants.

From previous works[7~9], the burning rate of inert polymer/nitramine propellants was also found to depend mainly on the heat released at the burning surface. On the basis of these results, it is found that the combustion process of the azide/nitramine propellants is similar to that of inert polymer/nitramine propellants. However, the ratio of the heat flux transferred back from the gas phase to the burning surface to the heat flux released at the burning surface for azide/nitramine propellants is less than that for inert polymer/nitramine propellants. The ratio are 0. 03 for azide/nitramine propellants and 0. 1 for inert polymer/nitramine propellants. The difference of the ratio between azide/nitramine and inert polymer/nitramine propellants is supposed to be caused by the exothermic reaction of AMMO at the burning surface.

Conclusions

The burning rate characteristics of azide/nitramine propellants were studied in order to gain a wide spectrum of burning rate. The burning rate of AMMO/EDNA propellant is higher than that of AMMO/HMX propellant and the pressure exponent of AMMO/EDNA propellant is lower than that of AMMO/HMX propellant. Both AMMO/EDNA and AMMO/HMX propellants exhibit the same combustion wave structure as inert polymer/nitramine propellants.

The burning surface temperature and the temperature at the end of the first-stage reaction zone for AMMO/EDNA and AMMO/HMX propellants are approximately the same in the pressure range between 1. 0 and 5. 0 MPa. The heat released at the burning surface for AMMO/EDNA propellant is larger than for AMMO/HMX propellant. The experiments indicate that the burning rate of AMMO/EDNA propellant depends mainly on the heat released at the burning surface.

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高エネルギーコンポジット推進薬の燃焼機構(第5報)
ーアジ化ポリマ/ニトラミン系推進薬の燃焼ー

馬崎　運*，飯田章英*，御手洗善昭*

アジド/ニトラミン系推進薬の燃焼速度機構を研究するために熱電対を用いて燃焼波構造を調べた。実験より，AMMO/EDNA推進薬の燃焼速度はAMMO/HMX推進薬より速く，AMMO/EDNA推進薬の圧力指数はAMMO/HMX推進薬より低いことが確認された。これら推進薬の燃焼波の温度プロフィールの測定結果より，燃焼表面で発生する熱流束が気相から燃焼表面への熱流束より大きいことが確認された。AMMO/EDNA推進薬とAMMO/HMX推進薬の燃焼速度に対しては，主に燃焼表面での発熱反応が影響を与えていることがわかった。AMMO/EDNA推進薬の燃焼速度がAMMO/HMX推進薬より速いのは，燃焼表面における発熱量がより大きいことによると考えられる。

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