Chemistry of an aluminized ammonium nitrate based HTPB composite solid propellant combustion

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The chemistry of an aluminized ammonium nitrate based hydroxy terminated polybutadiene (HTPB) composite solid propellant combustion was studied in this report. When ammonium perchlorate was added to an ammonium nitrate based HTPB composite solid propellant, which consisted of ammonium nitrate, aluminum and HTPB binder (A^3NPL propellant), enhancement of the aluminum oxidation process occurred which was determined by quantitative analysis of the unreacted aluminum.

The roles of magnesium when added to an A^3NPL propellant are (1) an enhancement of the aluminum oxidation process and (2) a neutralization of the acidic exhaust. For the latter case, two stepwise reaction sequences, which includes Eq. 3 followed by Eq. 4, is applicable for calculating magnesium demand that inhibits acidic exhausts.

1. Introduction

The current practical solid rocket propellant for nonmilitary use consists of oxysalts as an oxidizer, hydroxy terminated polybutadiene (HTPB) serving as the fuel and binder, aluminum powder as an energetic material, combustion catalysts and so on. Although ammonium perchlorate (AP) has been mainly used as an oxidizer in solid rocket propellants, it has a problem of air pollution and ozone destruction in the stratosphere because of hydrochloric acid or other chlorine compounds in the combustion gases. Adoption of ammonium nitrate (AN) as an oxidizer in place of ammonium perchlorate is a candidate to decrease the amount of acidic rain caused by launching of a rocket. But if use ammonium nitrate as an oxidizer, it is known that there is insufficient oxidation of the aluminum powder which is used as the energetic material because of the low combustion temperature and noncorrosive properties of the product gases to aluminum compared with ammonium perchlorate.

At the present time, a propellant formulation which contains ammonium nitrate as an oxidizer is the most practical based on the low acid exhaust and cost performance. From these circumstances, there are some ideas to improve ammonium nitrate containing rocket propellants. First is the use of the ammonium nitrate – ammonium perchlorate mixtures which are prepared by substitution of part of the ammonium nitrate by ammonium perchlorate to minimize acid pollutants and to enhence combustion efficiency[1]. The other is the idea of a "Mg – containing propellant" which is intended to neutralize acid exhaust by reaction with the alkaline combustion product of magnesium[2]. Iwama et. al. reported the combined method of the above using GAP binder[3].

In this experiment, the problems of the solid propellant which contain ammonium nitrate, ammonium perchlorate and aluminum (A^3NPL propellant) with magnesium were discussed in order to clarify the combustion chemistry of solid propellant proposed by Iwama et. al. At first, the effect of ammonium perchlorate substitution for part of the ammonium nitrate

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Table 1 Propellant formulations

	HTPB	Al	Mg	AN	AP
AN 14	20	14	0	66	0
AN 16	20	14	0	56	10
AN 17	20	14	0	46	20
AN 18	20	14	0	36	30
AN 19	20	8	0	52	20
AN 20	20	24	0	36	20
AN 24	20	7	7	56	10
AN 25	20	7	7	46	20
AN 26	20	7	7	36	30
AN 27	20	7	7	66	0
AN 28	20	12.6	1.4	46	20
AN 29	20	9.8	4.2	46	20
AN 30	20	12.6	1.4	66	0
AN 31	20	9.8	4.2	66	0

HTPB:hydroxy terminated polybutadiene binder,
AN:ammonium nitrate, AP:ammonium perchlorate,
Al:aluminum, Mg:magnesium

in an ammonium nitrate based solid propellant on aluminum oxidation was studied by thermal analysis, quantitative analysis of the unreacted aluminum and combustion calorimetry. Next, combustion efficiency and acid formation were evaluated when magnesium was added as magnalium to the A^{3}NPL propellant. Moreover, the reaction equation was established for the combustion of a"Mg−containing A^{3}NPL propellant".

2. Experimental

2.1 Materials A^{3}NPL

Reagent grade ammonium nitrate, purified from water, was pulverized and screened into under 147 μm(100 mesh pass)after sufficient drying. The aluminum used was commercially atomized powder and was pulverized to about 10 μm.

Magnesium was a commercial reagent grade powder. Magnalium was prepared by the mechanical alloying of aluminum and magnesium powder in which the magnesium contents were 10, 30 and 50 wt.%. Its mean particle sizes were about 10μm.

Two types of propellant were prepared. The first group was magnesium−free propellants and the second was a magnesium−containing one. In each case, the HTPB content was determined to be 20 wt.%. Magnesium was contained as magnalium. These propellant formulations are described in Table 1.

2.2 Thermal analysis

The oxidation of aluminum, magnesium and magnalium by atmospheric oxygen and the reaction with ammonium nitrate were studied by thermal analysis. Thermal analysis during oxidation was carried out for the sample packed in alumina crucibles using a simultateneous DTA−TG apparatus. In the reaction with ammonium nitrate, the thermal analysis was carried out in an argon gas atmosphere using a high−pressure DTA apparatus with hermetically sealed aluminum crucibles which have pinholes in the center of their cover. In each case, the sample weight was 5 mg and the heating rate was 20 K/min.

2.3 Measurement of the heat of reaction

The heat of reaction was measured under a pressurized argon condition of 2 MPa by a bomb colorimeter with about 2.0 g of propellant. One−tenth gram of the mixture of boron and bariumchromate (B/BaCrO$_4$ = 13/87 by weight)was used as the initiator to easily ignite the mixture.

2.4 Determination of the extent of oxidation

The fractional oxidation of aluminum after combustion was determined using a volumetric method in which the volume of hydrogen gas evolved by the reaction of the unreacted aluminum in the combustion

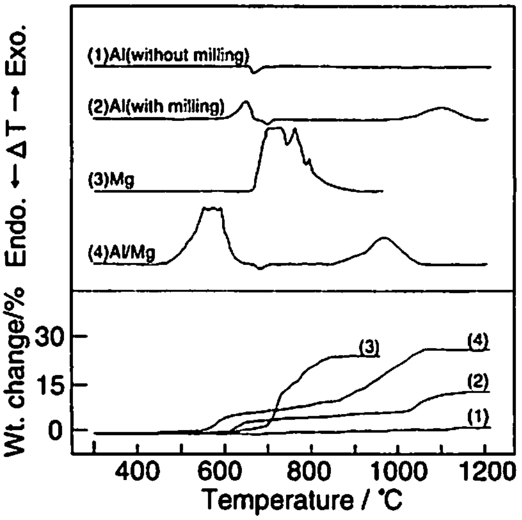

Fig. 1 Thermal analysis of aluminum, magnesium and magnalium in air.

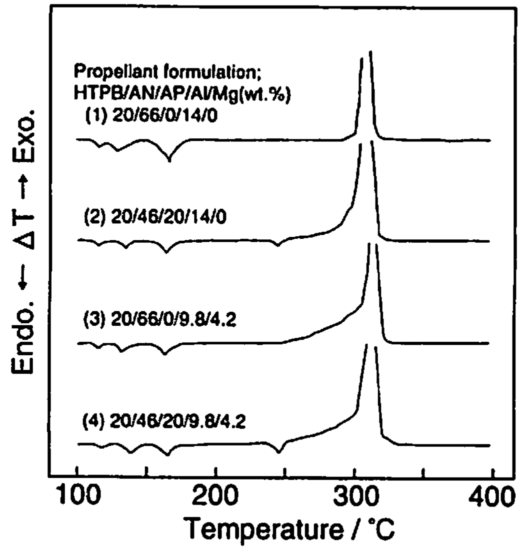

Fig. 2 DTA curves of ammonium nitrate composite propellant containing aluminum,magnesium and ammonium perchlorate.

residue with added 8 N−hydrochloric acid was measured. A preliminary experiment shows that the relative deviation of this method is within ± 2 %.

2.5 Determination of acidity

In an airtight container 2.35 g of propellant was burned under a pressurized condition of 2 MPa argon. The amount of acid of the combustion product after burning was dissolved in 500 ml of distilled water and directly determined by pH titration, in which the neutralizing point was taken as pH=5.8. Any gaseous acid product was determined by the same method after being dissolving in 200 ml of distilled water.

3 Experimental Results

3.1 The thermal reactivity of aluminum, magnesium and magnalium, and its mixture with ammonium nitrate

Figure 1 shows the results of the thermal analysis of aluminum, magnesium and magnalium in air or argon. The oxidation with regard to aluminum without milling commenced at 624 ℃ before melting (mp−660℃) and that with milling at 573 ℃. But the extent of oxidation was not very large. The fractional oxidation of aluminum powder without milling was 9.4 wt.% and for the milled one it was 35.3 wt.% by heating in air up to 1200℃. The oxidation of magnesium in air began at 483℃ before melting(mp−650℃) and was thoroughly oxidized at 800 ℃. On the other hand, the oxidation of magnalium commenced at a lower temperature which is in the neighborhood of its eutectic point. Magnalium, which containes 50 wt.% magnesium began to show an exothermic reaction at about 400 ℃ before melting(eutectic point of this magnalium is 460 ℃). Every magnalium showed a high fractional oxidation though its extent differed with magnesium content. That is, the fractional oxidation for 10, 30 and 50 wt.%−magnesium are 90.8, 100 and 100% by weight, respectively.

Figure 2 shows the results of the thermal analysis for aluminized ammonium nitrate based hydroxy terminated polybutadiene composite solid propellants with and without magnesium in argon atmosphere. The addition of ammonium perchlorate to aluminized ammonium nitrate based hydroxy terminated polybutadiene propellant(A^{3}NPL propellant)showed an exothermic peak temperature drop of 10 ℃ compared to the one without ammonium perchlorate. This indicates some catalytic action of ammonium perchlorate on the thermal reaction of the propellant. Thermoanalytically, the addition of magnesium does not cause a remarkable difference in the thermal reactivity of the A^{3}NPL propellant.

3.2 Heat of reaction and the extent of oxidation of aluminum

Figure 3 shows the effect of ammonium perchlorate on the heat of reaction of the aluminized am-

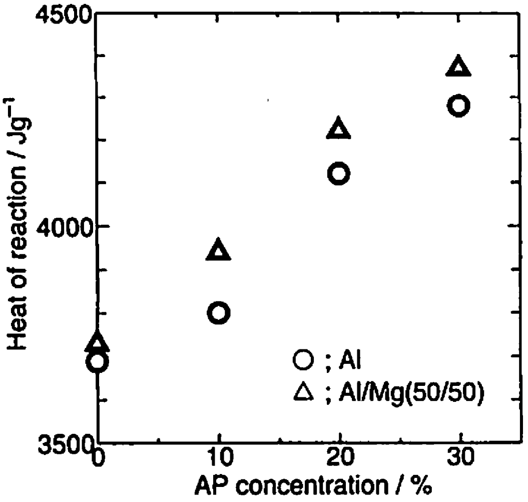

Fig. 3 Effect of ammonium perchlorate on the heat of reaction of aluminized ammonium nitrate composite propellant.

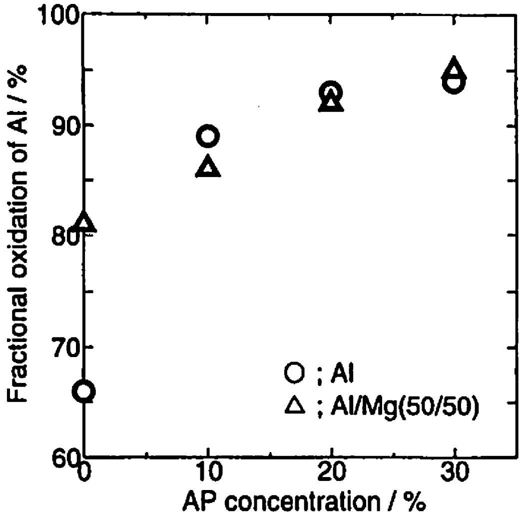

Fig. 4 Effect of ammonium perchlorate on the oxidation of aluminum in ammonium nitrate composite propellant.

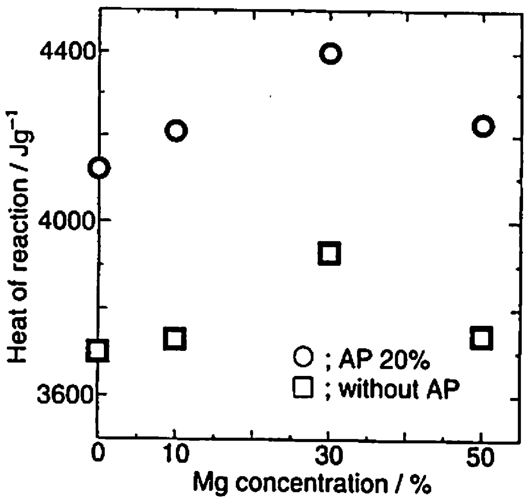

Fig. 5 Effect of magnesium on the heat of reation of ammonium nitrate composite propellants.

monium nitrate based HTPB solid propellant without and with magnesium. From these results, it was found that the propellants with magnesium had a larger heat of reaction than that without magnesium and the heat of reaction became larger according to ammonium perchlorte content. Fig. 4 shows the effect of ammonium perchlorate on the fractional oxidation of aluminum for the propellants with (50 wt. %) and without magnesium. From this result, we can conclude that about a 20 wt. % addition of ammonium perchlorate was sufficient in order to enhance the extent of oxidation, because propellants with and without magnesium had a fractional oxidation of about 95 wt. %.

Every heat of reaction became larger with ammonium perchlorte content. But, the propellant with magnesium had a better oxidation efficiency than that without mgnesium, which contained no ammonium perchlorate. Comparing this result with the heat of reaction in Fig. 3, it was determined that there is no difference in the heat of reaction, even though there is a considerable difference in the fractional oxidation of aluminum. This is because the propellant is usually formulated in order to perform under a fuel rich condition, and other reducing species such as hydrogen are oxidized instead of aluminum. If ammonium perchlorate exceeded to 20 wt. %, the fractional oxidation of aluminum showed the same value for the propellant with and without magnesium.

Figure 5 shows the effect of magnesium content on the heat of reaction of the magnesium-containing A^3 NPL propellants and propellants without ammonium perchlorate. Propellants with and without ammonium perchlorate shows the maximum heat of reaction value at 30 wt. % magnesium content. But A^3NPL propellants, in which the ratio of ammonium nitrate and ammonium perchlorate is 80 : 20 (by weight), shows larger heat of reaction values than that of propellants without ammonium perchlorate. This result is ascribed to the extent of aluminum oxidation in the

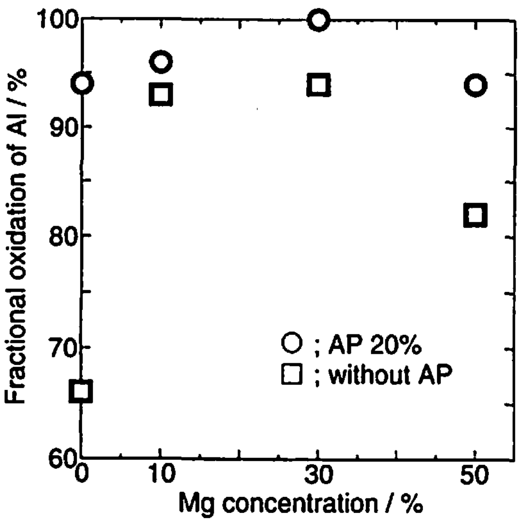

Fig. 6 Effect of magnesium on the oxidation of aluminum in ammonium nitrate composite propellants.

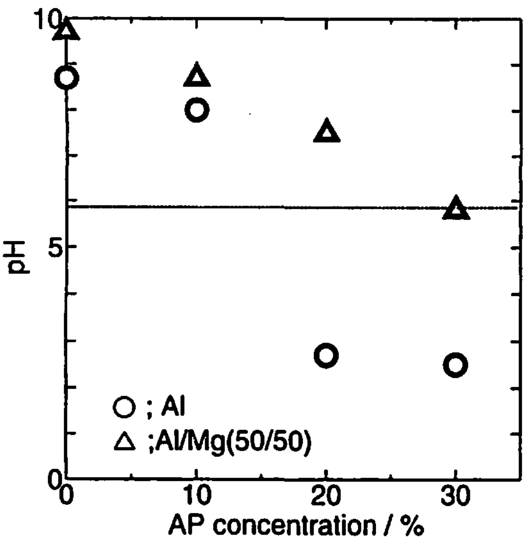

Fig. 7 Effect of ammonium perchlorate on acidity of the residue after the combustion of ammonium nitrate composite propellants.

propellants. The fractional oxidation of aluminum in Fig. 6 corresponds well with the heat of reaction result.

3.3 Acidity of the combustion products

The combustion products of the mixture of ammonium nitrate and aluminum, though its composition depends on the propellant formulation, are water, nitrogen, oxygen, hydrogen, nitrogen oxide, ammonia and aluminum oxide. The A^3NPL propellant, in addition to the above products, forms carbon monoxide, carbon dioxide, hydrochloric acid and some hydrocarbons, though its distribution depends on the propellant formulation. The acid substances among these products are hydrochloric acid, nitrogen oxide and carbon dioxide. The gaseous product contains nitrogen oxide and carbon dioxide as acidic substances. But, most of the acidic substances such as hydrochloric acid and aluminum oxide exist in the condensed phase because these were dissolved in or coexist with the produced water.

The volume of titration of the condensed phase is larger by about ten times than that of the gaseous phase, the neutralizing point being taken at pH 5.8. From x-ray powder diffraction data of the combustion products in condensed phase that had been dryed at 120℃, magnesium aluminate was found to exist.

Figure 7 shows the effect of ammonium perchlorate on the amount of acid in the condensed phase after the combustion of the solid propellant with 50 wt.% magnesium and without magnesium. The condensed phase for the propellants without ammonium perchlorate (AP content equals zero in Fig. 7) had an alkaline property whether magnesium was contained or not. With regard to the propellants which contained ammonium perchlorate, propellants with magnesium had higher pH values than that without magnesium. Futhermore, it was determined that the pH values decreased according to the ammonium perchlorate content. Especially, propellants without magnesium showed a low pH value when ammonium perchlorate exceeded 20 wt.% in content. The amount of gaseous acid products absorbed in the distilled water showed the same tendency as that in the condensed phase.

Figure 8 shows the effect of the addition of magnesium on the amount of acid in the condensed phase after the combustion of the A^3NPL propellants. The A^3NPL propellant without magnesium formed acidic condensed products. With regard to the A^3NPL propellants with magnesium, in which the ratio of ammonium nitrate and ammonium perchlorate is 80 : 20 (by weight), the condensed products had an acidic nature up to a magnesium content of 30 wt.% and an alkaline nature over this value. Gaseous acid products absorbed in distilled water were neutral regardless of

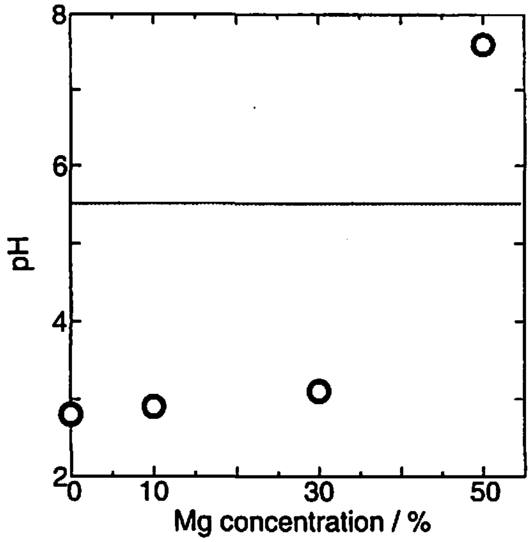

Fig. 8 Effect of magnesium on acidity of the residue after the combustion of AP 20% containing ammonium nitrate composite propellants.

magnesium content.

4. Discussion

Propellants, which consist of ammonium nitrate, HTPB binder and aluminum, have a problem of insufficient oxidation of aluminum because of the lower combustion temperature and reaction resistance of the surface oxide layer of aluminum. If ammonium perchlorate is added to these formulations(A^3NPL propellant), the extent of aluminum oxidation goes up because of an increase in the combustion temperature and the corrosive property of hydrogen chloride gas produced versus the oxide layer of aluminum. In this experiment, it was determined that about a 20 wt.% content of ammonium perchlorate showed sufficient oxidation efficiency if the mixture of ammonium nitrate and ammonium perchlorate was used as the oxidizer. But, these propellants which contained 20 wt.% ammonium perchlorate as the oxidizer produced about 1.00×10^{-3} moles acid per gram propellant.

Magnesium is added to the A^3NPL propellants to lower the level of acidic exhaust. In this experiment, the A^3NPL propellants with magnesium also produced a lower level of acidic exhaust compared to one without magnesium. The addition of magnesium caused another improvement effect on the aluminum oxidation reactivity. In Fig. 4, propellants without ammonium perchlorate showed a remarkable increase in the fractional oxidation with a small addition of magnesium. From the thermal analysis, it was found that magnalium had a higher oxidation reactivity. This is because magnesium has a higher oxidative property and that magnesium oxide removed the aluminum oxide layer to allow a reaction with aluminum oxide on its surface by the formation of magnesium aluminate. But, when the amount of magnesium exceed 30 wt.%, the heat of reaction of the propellants decreased, because the heat of formation of magnesium oxide per unit weight is smaller than that of aluminum.

From Fig. 8, with regard to the A^3NPL propellants, in which the ratio of ammonium nitrate and ammonium perchlorate is 80 : 20 (by weight), we can conclude that the addition of over 30 wt.% magnesium is needed to obtain a clean exhaust. This is interpreted as follows. Aluminum and magnesium react with oxygen produced by the thermal decomposition of oxidizers in the propellant according to Eqs. (1) and(2). Alkaline oxidation products of magnesium such as magnesium oxide or magnesium hydroxide(formed by the reaction of the water combustion product)both react with aluminum oxide to form magnesium aluminate and then react with hydrogen chloride, as shown in Eqs. (1) – (5).

$$2Al+3/2O_2=Al_2O_3 \quad (1)$$

$$Mg+1/2O_2=MgO \quad (2)$$

$$MgO+Al_2O_3=MgAl_2O_4 \quad (3)$$

$$MgO+2HCl=MgCl_2+H_2O \quad (4)$$

$$Mg(OH)_2+2HCl=MgCl_2+2H_2O \quad (5)$$

But, because both of the reaction products of magnasium and aluminum closely exist to each other under combustion circumstances of the propellant, the alkaline magnesium oxidation product, MgO, reacts at first with the acidic aluminum oxide. In this experiment, the amount of magnesium to complete the above reaction (3) was calculated to be about 30 wt.% magnesium. Once the aluminum oxide was consumed, hydrochloric acid was neutralized and more than 7 wt.% magnesium was needed to complete reactions (4) or (5) from calculation of the ammonium perchlorate content. So, A^3NPL propellants with magnesium, in which the ratio of ammonium nitrate and ammonium perchlorate is 80 : 20 (by weight), requires about 38 wt.% magnesium content to neutralize the acid product gases. This two−step consideration including Eq. (3) followed by Eq. (4) to calculate magnesium demand is applicable to all the other compositions of A'NPL propellant to formulate non−acidic exhaust gases using magnesium.

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硝酸アンモニウム－アルミニウム－HTPB系固体推進薬燃焼の化学

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硝酸アンモニウム，過塩素酸アンモニウム，アルミニウム，マグネシウム，HTPBバインダーから成る固体推進薬の燃焼の際に起る化学反応が検討され，以下の結果が得られた。

Alの一部に代り加えられたマグネシウムはアルミニウムの酸化を促進し，生成した酸性ガスを中和する。この化学反応は二段階の反応によって進行する。また，アルミニウムの代りにマグネシウムを用いても，燃焼熱等の燃焼性能は低下せず，むしろアルミニウムの酸化率の向上などにより高性能化した。

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