Effect of additives on the reaction of the mixtures of ammonium nitrate with aluminum

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Aluminum powder in explosive mixtures is difficult to react completely because of its stable surface oxide layer, especially, if ammonium nitrate is used as the oxidizer where the combustion temperature is relatively low. In this report, the effects of various additives on the reaction of ammonium nitrate with aluminum were studied by thermal analysis, combustion calorimetry and analyses of the reaction residue.

The mixtures of ammonium nitrate with aluminum without additives could not produce complete combustion. But, the mixtures with some additives such as cryolite could produce a complete combustion reaction and a perfect oxidation of aluminum were obtained for the 70 : 30 mixture (by weight) of ammonium nitrate with aluminum. Moreover, obtained heat of combustion and amount of water produced corresponded to the calculated one according to equation (4)

1. Introduction

The reaction of ammonium nitrate (described as "AN") with aluminum is important in some types of explosive mixtures such as in industrial explosives or in composite solid propellants. In the combustion of aluminium powder in an explosive mixture, the reaction of aluminum with gaseous oxygen or an oxidizer is interupted in the course of the reaction by a stable oxide layer that forms on its surface. Moreover, if we use ammonium nitrate as an oxidizer, aluminum powder is difficult to react completely, because of the relatively low combustion temperature. It is known that this surface oxide layer is weakened by corrosive materials. For example, addition of ammonium perchlorate to a solid propellant, which contains ammonium nitrate as a main oxidizer, enhances the extent of oxidation of aluminum by corrosion caused by the chlorine compounds in the product gases[1].

In molten salt electrolysis of aluminum, a technique of fusing agents has been utilized to lower the melting point. So, fusing mixtures such as a cryolite, if added to the mixtures of ammonium nitrate with aluminum, can be considered to eliminate the surface oxide layer on the aluminum and enhence the extent of aluminum oxidation. In this paper, the effects of various additives on the reaction of ammonium nitrate with aluminum were studied by thermal analysis, combustion calorimetry and analyses of reaction residue.

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2. Experimental

2.1 Materials

Reagent grade ammonium nitrate, purified from water, was pulverized and screened through 147 μm (100 mesh pass) after sufficient drying. The aluminum used was a pigment type powder ("p-Al") and was surface-treated with stearic acid (2 wt. %) and teflon (0.15-0.25 wt. %).

The composition of the additives is described in Table 1. All these materials were prepared after pulverizing the reagents and passing through a 74μm sieve (200 mesh pass).

2.2 Thermal analysis

Thermal analyses were carried out under an argon gas atmosphere with a RIGAKUDENKI high-pressure

Table 1 Composition of additives (wt. %)

	KCl	NaCl	Na_3AlF_6	others
No. 1	50	40	8	AlF_3 1.2, LiCl 0.8
No. 2	30	30	–	LiCl 10, KBr 10 KI 10, NaF 10
No. 3	40	30	10	$ZnCl_2$ 20
cryolite	–	–	100	

DTA, simultaneous DTA–TG and DSC apparatus. As the sample container, a hermetically sealed aluminum crucible which had a pinhole in the center of the cover was used for simple ammonium nitrate and its mixtures with aluminum. An iron sealed container without a pinhole was used for DSC experimentation and alumina crucibles were used for the oxidation of aluminum in air. In each case, the sample weight was about 5 mg and the heating rate was 10–20 K/min.

2.3 Measurement of the heat of reaction

The heat of reaction with 1g of the weighed mixture of ammonium nitrate and aluminum in argon was measured with a SHIMADZU combustion colorimeter. A mixture (0.1g) of boron and barium chromate ($B/BaCrO_4$ = 13/87 by weight) was used to initiate the reaction more readily.

The weight of reaction residue in condensed phase, the extent of oxidation, and the water produced were determined after the combustion experiment was carried out. In these experiments, aluminaballs were used in the bomb to suppress the scatter of the sample.

2.4 Determination of the fractional oxidation of aluminum

The fractional oxidation of aluminum after combustion was determined by a volumetric method, which measures the volume of hydrogen gas evolved by the reaction of the unreacted aluminum in the combustion residue with added 8N–hydrochloric acid. Preliminary experimentation has shown that the relative deviation of the amount of unreacted aluminum by this method is within ±2%.

2.5 Qualitative and quantitative analyses of the reaction residue

The amount of water produced by combustion was determined by gaschromatography after adding and mixing well the combustion product with 50 ml of methanol. The packing reagent was PEG 1000 and the column temperature was 100℃. The relative deviation by this method is within ±1%.

Qualitative and quantitative analyses of unreacted ammonium nitrate were performed using common X–ray powder diffraction and absorbtiometry after dissolution in water.

3. Results and Discussion

3.1 Thermal properties of ammonium nitrate, aluminum and their mixtures

Fig. 1 shows the results of the DTA curves of ammonium nitrate under pressures ranging from normal to 10 MPa (gauge). Ammonium nitrate under normal pressure shows only an endothermic reaction resulting from a phase transformation and evaporation on heating. However, above 0.5 MPa (gauge) an

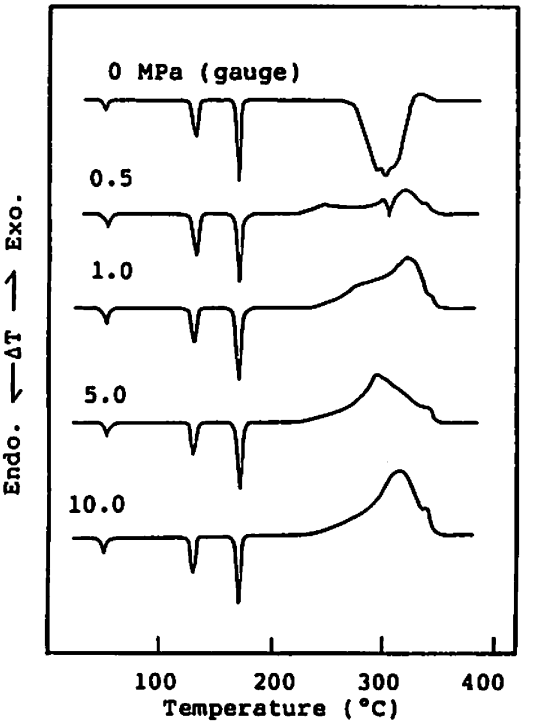


Fig. 1 DTA curves of ammonium nitrate under pressurized conditions

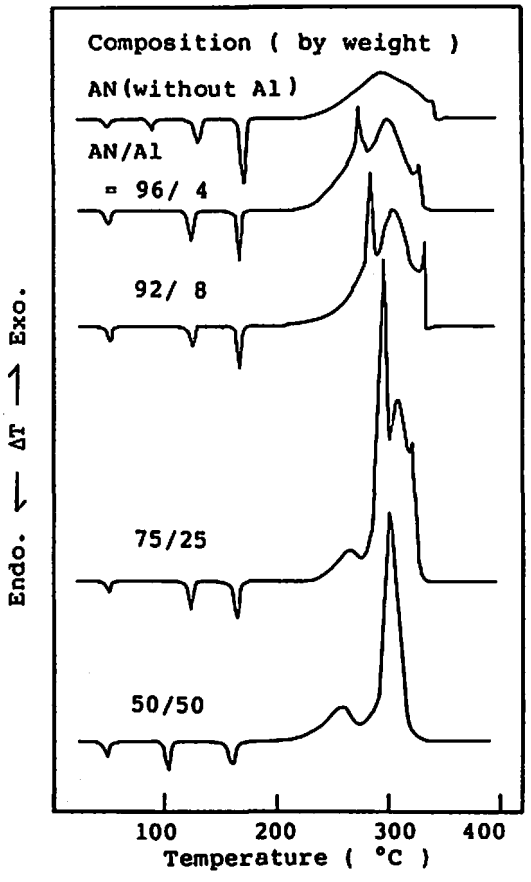


Fig. 2 DTA curves of the mixture of ammonium nitrate with aluminum under a pressure of 5.0 MPa(gauge)argon

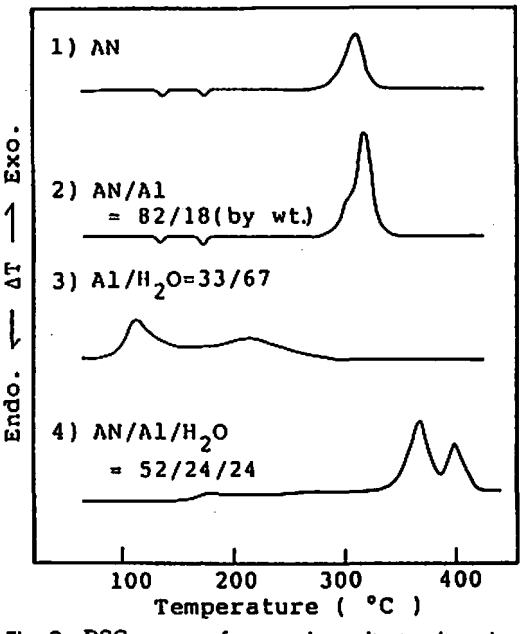


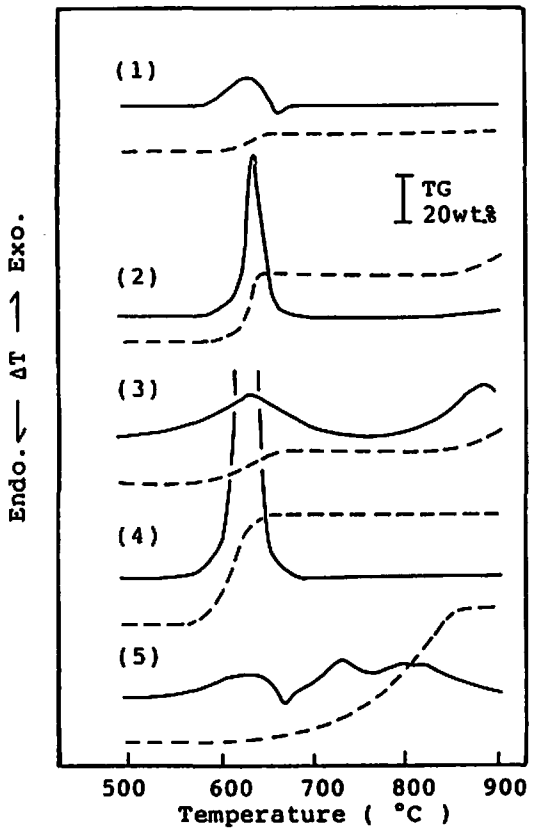
Fig. 3 DSC curves of ammonium nitrate, its mixture with aluminum without and with water, and the mixture of aluminum with water

Table 2 Effect of addition of aluminum and water on the heat of reaction for ammonium nitrate obtained from the DSC study

Reactant(by wt.)	$-\Delta H$(J/g)
AN	1204
AN/Al(82/18)	2358
Al/H_2O(33/67)	1693
$AN/Al/H_2O$(52/24/24)	3373

exothermic reaction appeared as a result of restraining evaporation. Therefore, a pressurized condition above 5 MPa(gauge)was adopted in order to examine the reactivity of ammonium nitrate in thermal analysis. Fig. 2 presents DTA curves of the various mixtures of ammonium nitrate with aluminum under 5 MPa(gauge). Every mixture had 2−4 exothermic peaks, which indicates a larger exothermicity compared to ammonium nitrate alone. Hence, we can conclude that the oxidation of aluminum occurred under this condition. Howevere, to what extent the aluminum was oxidized could not be determined from these experiments.

In order to examine the extent of the aluminum oxidation under the different conditions, thermal analyses were carried out using a sealed container, which would restrain mass transfer. Fig. 3 and Table 2 show the results of the DSC studies for ammonium nitrate, its mixtures with aluminum or water (reaction product of ammonium nitrate)and the mixture of aluminum with water. Under this condition, both the decomposition of ammonium nitrate and its reaction with aluminum started at a somewhat higher temperature, and the value of the heat of reaction shows the occurrence of an imperfect reaction if we consider the reaction equations shown as(1) and(2). Fig. 3−3 and Fig. 3−4 show the effect of water, the reaction product of ammonium nitrate, on the oxidation of aluminum. The reaction of aluminum with water started at 91℃, and the extent of aluminum oxidation was estimated at about 20% from the exothermicity and the calculated heat of reaction(ΔH)for



——; DTA, ----; TG,
additive (p-Al/additive=4/1 wt.)
(1) without additive, (2) No.1,
(3) No.2, (4) No.3, (5) cryolite

Fig. 4 DTA and TG curves of aluminum with and without additives

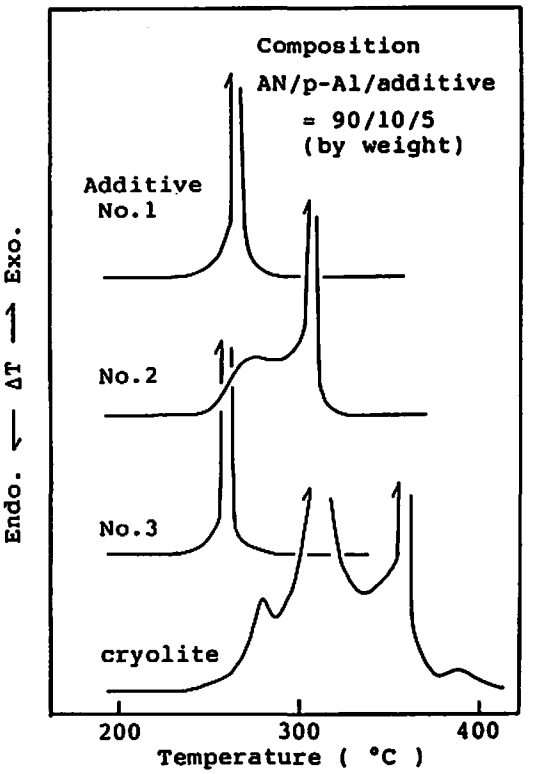


Fig. 5 DTA curves of the mixture of ammonium nitrate, aluminum and additives under a pressure of 0.5 MPa(gauge)argon

equation(3). Water also had an effect on the reaction of the mixture of ammonium nitrate with aluminum based on the large exothermicity obtained(Fig. 3−4).

$$NH_4NO_3 \rightarrow N_2+2H_2O+1/2O_2 \qquad \Delta H_1=-1450J/g \quad (1)$$

$$2Al+3NH_4NO_3 \rightarrow Al_2O_3+6H_2O+3N_2 \qquad \Delta H_2=-6880J/g \quad (2)$$

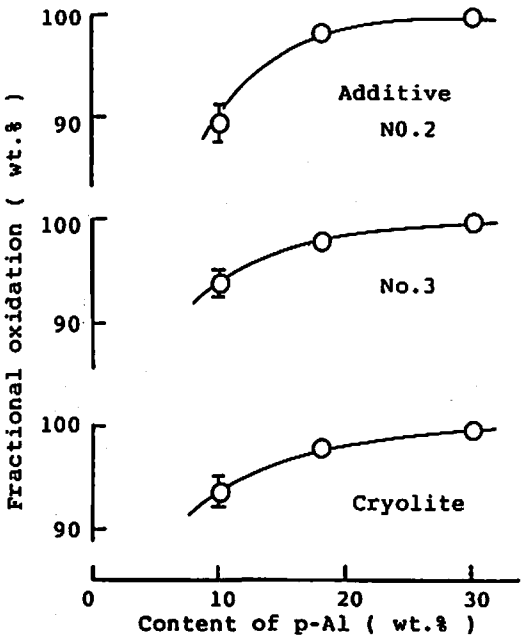
$$2Al+3H_2O \rightarrow Al_2O_3+3H_2 \qquad \Delta H_3=-8733J/g \quad (3)$$

3.2 Effect of additives on the thermal reactivity of aluminum powder and its mixtures with ammonium nitrate

Fig. 4 shows the results of the thermal analyses for aluminum with and without additives. Aluminum without additives gradually suffered oxidation before the melting point(melting point:660℃) and showed about 10% increase in weight up to 900℃. The fractional oxidation up to this temperature was estimated at about 11%, compared to complete oxidation in which the weight increase amounted to 88.9%.

On the other hand, the additives had a remarkable promoting effect on oxidation. For example, additives no. 1 and no. 3 promoted oxidation around 600℃, and additives no. 2 and cryolite had moderate effects on the promotion of oxidation over a wide range of temperatures. The most effective additive was cryolite, which showed an 58% increase in weight at 900℃. This weight increase corresponded to a fractional oxidation of 65%.

Fig. 5 shows the DTA curves of the mixture of aluminum, ammonium nitrate and the additives. The mixture was formulated so that the additives were added by 5 wt% increments to the binary mixture of ammonium nitrate and aluminum having a composition of 90 parts of ammonium nitrate and 10 parts of aluminum. Experiments were carried out under pressurerized conditions with argon in order to avoid



The ratio of the mixture / additive; 100:3 in weight

Fig. 6 Fractional oxidation of aluminum from the mixture of ammonium nitrate and aluminum with additives under a pressure of 2.0 MPa(gauge)argon

the effect of atmospheric oxygen and the evaporation of ammonium nitrate. The DTA curves showed that addittives No. 1 and No. 3 caused a sharp exothermic peak at 250℃ ; whereas, cryolite and No. 2 caused a broad one. It is known that the halide ion promotes the thermal decomposition of ammonium nitrate[2]. These results indicate that a sharp and large exothermic reaction is possible because of the promoting effects of halide on the thermal decomposition of ammonium nitrate.

3.3 The extent of the oxidation of aluminum in the reaction of ammonium nitrate with aluminum

The combustion experiments for the ammonium nitrate−aluminum mixtures with 3% additives were carried out in order to determine the extent of the oxidation of aluminum. Fig. 6 shows the fractional oxidation of aluminum detected in the combustion residue. In this figure, all the values accompanied by mean deviations are the average of three experiments. The mixtures of ammonium nitrate and aluminum without additives were not ignited even though under usage of an igniter. With regard to composition, the higher the content of aluminum, the higher the fractional oxidation became. But, the mixtures containing aluminum above 40 wt. % did not ignited.

Table 3 Heat of reaction for the mixtures of NH_4NO_3/p−Al/additives

additives	composition(by wt.)		
	70/30/ 3	82/18/ 3	90/10/ 3
No. 2	8556	7141	4357
	8550	7218	4420
	8434	7205	4623
	8471	7129	4801
No. 3	8506	7204	4853
	8514	7235	4745
	8520	7098	4745
	8492	7174	4697
cryolite	8411	7143	4772
	8514	7043	4508
	8481	7210	4508
	8481	7143	4601

The results obtained above indicate that the additives promote the oxidation of aluminum. For example, the mixtures of ammonium nitrate, aluminum and additives in a ratio of 70 : 30 : 3 and 82 : 18 : 3 (by weight) showed a fractional oxidation over 99.5% and 98.0%, respectively. These values differed very little between additives and the deviations were also very small. The weight of the residue after combustion corresponded well to the sum of aluminum oxide and the additives. However, a mixture of ammonium nitrate, aluminum and additive in the ratio of 90 : 10 : 3 (by weight) showed 10% smaller weight decrease than the calculated value(80%) . This indicates incomplete decomposition of the ammonium nitate, which was actually detected in the combustion residues by X−ray powder diffraction.

3.4 Equation of the reaction of ammonium nitrate with aluminum

After combustion of the 70 : 30 mixture of ammonium nitrate and aluminum with 3 % additive, it was found that there were a compleate oxidation of aluminum, a compleate decomposition of ammonium nitrate, initial additive remained unchanged and a large amount of water formation(Table 4). So, suppo-

Table 4 Amount of H_2O formed from mixture of NH_4NO_3/p−Al/cryolite

composition (by wt.)	H_2O formed	
	g/g*	mol/ 2 Al
70/30/ 3	0.155	1.55
	0.152	1.52
	0.146	1.46
average	0.151	1.51
82/18/ 3	0.323	5.21
	0.313	5.34
	0.320	5.32
average	0.319	5.30

*g/g(NH_4NO_3+Al)

sing the aluminum was thoroughly oxidized and ammonium nitrate completely decomposed, the reaction equation between aluminum and ammonium nitrate for the 70 : 30, 82 : 18 and 90 : 10 ammonium nitrate/aluminum mixtures can be described as follows.

$$1.57NH_4NO_3+2.00Al \rightarrow 1.75N_2+1.43H_2+1.71H_2O+1.00Al_2O_3 \quad (4)$$
$$(\Delta H_4=-8410J/g)$$

$$3.07NH_4NO_3+2.00Al \rightarrow 3.07N_2+0.07O_2+6.14H_2O+1.00Al_2O_3 \quad (5)$$
$$(\Delta H_4=-6779J/g)$$

$$6.07NH_4NO_3+2.00Al \rightarrow 6.07N_2+3.07O_2+12.14H_2O+1.00Al_2O_3 \quad (6)$$
$$(\Delta H_4=-4424J/g)$$

Table 3 shows the heat of reaction for the three mixtures of ammonium nitrate, aluminum, and the additives in argon. The heat of reactions estimated with regard to the above reactions were described in the bracket of the above eqution(ΔH_4, ΔH_5 and ΔH_6) and corresponded well to the measured value in Table 3. As described above, the mixture which contains excess ammonium nitrate had very little effects on the oxidation, and the heat of reaction was somewhat small because part of the ammonium nitrate did not react.

Table 4 shows the ammount of water evolved from the combustion reaction, in which the aluminum was almost completely oxidized. The observed amounts of water for 70 : 30 : 3 and 82 : 18 : 3 mixtures in Table 4 are 88% and 87% of the calculated values from equation(4) and(5).

Conclusions

The mixtures of ammonium nitrate with aluminum without additives could not produce combustion; however, the mixtures with some additives, which can eliminate the surface oxide layer, could produce a complete combustion reaction and so a perfect oxidation of aluminum, if suitable mixture compositions and additives were selected. The observed heats of reaction for the 70 : 30 : 3, 82 : 18 : 3, 90 : 10 : 3 ammonium nitrate/aluminum/additive mixtures during combustion were corresponded well to that obtained from the reaction equations(4), (5) and(6).

Refernces

1) Kazuo Miyauchi, Takahisa Yamasaki, Takuo Kuwahara and Naminosuke Kubota, J.Ind.Expl.Soc.JAPAN, 48.77 (1987)
2) Yasutake Hara, Hidetsugu Nakamura, Yoshikazu Hirosaki, Katsuhide Hattori and Hideyo Osada, J.Ind.Expl.Soc.JAPAN, 45.87 (1984)

硝酸アンモニウムとアルミニウムの混合物の反応性に及ぼす添加物の効果

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混合火薬に用いられるアルミニウム粉末はその表面に安定な酸化物層が存在するために完全には酸化されない。硝酸アンモニウムが酸化剤として用いられる場合には燃焼温度が比較的低いために，この傾向は特に顕著である。本研究では，硝酸アンモニウムを酸化剤，アルミニウムを還元剤として含む混合物中での硝酸アンモニウムとアルミニウムの反応性に及ぼす添加物の効果を，熱分析，燃焼熱の測定，反応残さの分析などを行なうことにより検討した。

硝酸アンモニウムとアルミニウムの混合物は添加物を加えない場合には本実験の条件下では着火しなかった。しかし，クリオライトなどアルミニウムの溶融塩電解工業で用いられる添加剤を添加すると燃焼は完結し，特に硝酸アンモニウムとアルミニウムの70：30の混合物ではアルミニウムはほとんど完全に酸化された。さらに，硝酸アンモニウムとアルミニウムの反応の実測された反応熱は仮定された反応式：（4），（5），（6）式からの計算値に良く一致した。

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