Research paper

A study on ammonium nitrate–metal nitrate double salts as oxidizers for gas generating agent

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Abstract

Aiming to take ammonium nitrate (AN) into conventional use as new oxidizer agent for gas generating agents on automobile airbag system, the combustion and thermal decomposition characteristics of gas generating agents consist of 5–amino–1–H–tetrazole (HAT), and AN were investigated. It was suggested that combustion performance of HAT/AN gas generating agent was improved by preparing AN into double salt with copper nitrate, or calcium nitrate. Combustion characteristics of gas generating agents consist of HAT, AN, and basic copper nitrate (BCN) was also investigated, and it was indicated that the addition of BCN to HAT/AN gas generating agents is effective to enhance their combustion characteristics.

Keywords : Ammonium nitrate, combustion, thermal analysis

1. Introduction

As the oxidizers for gas generating agents, metal nitrates, such as strontium nitrate, and metal oxides, such as copper oxide, are being used conventionally. Since these have oxidative properties, the gas generating agents, which contain these oxidizers,have appropriate combustion performance. However, metal nitrates and oxides have low gas generation efficiency, because of generation of the residual substances, which originate in metal elements. When the heat residual particles come out outside, there is a danger of making a hole in the airbag in the case of expansion and burdening the crew member with a burn. Although a reliable filter is needed in order to prevent the dangers, if the clogging of filter happens, it will lead to accidents, such as a burst of the inflator.

As the alternative material for metal nitrates oxidizers, ammonium nitrate (AN), which generates only clean gases (N_2, and H_2O) when perfect combustion is carried out, was thought to be ideal, and researches aiming practical use of AN as the oxidizer have been done. However AN cannot be used easily as it is, because of its poor properties, such as a low burning rate, phase transitions between solid phases at temperatures of practical use, and relatively higher hygroscopic property.

This study was conducted aiming at use of oxidizers containing AN as gas generating agent for air bags. As the fuel component for combustion experiments, 5–amino–1–H–tetrazole (HAT) was used. The improvement in combustion characteristics and phase stabilization of AN were attempted by the method of using double salts consist of AN, and some metal nitrates and discussed in this paper. And, combustion characteristics of gas generating agents consist of HAT, AN, and basic copper nitrate (BCN) mixture was also investigated

2. Experimental

2.1 Samples

Phase stabilization below 120°Cis required of gas generating agents for airbags. Therefore, the substances, which cause melting below 120°C, cannot be used. So, as a preliminary experiment, the samples, which are the double salt of one of six kinds of metal nitrates (nitrate of copper, calcium, strontium, zinc, nickel, and cobalt) and AN, were prepared and held for1hour in the thermostatic chamber

Table 1 Content of model gas generating agents for 52ml deflagration tests (wt.%).

sample	Fuel	Oxidizer				
	HAT	Cu $(NO_3)_2$	Ca $(NO_3)_2$	Sr $(NO_3)_2$	BCN	AN
HAT/AN	24.9	–	–	–	–	75.2
HAT/CuAN6	29.5	19.8	–	–	–	50.7
HAT/CaAN6	29.3	–	18.0	–	–	52.7
HAT/SrAN6	27.9	–	–	22.1	–	50.1
HAT/AN/BCN2.5	23.2	–	–	–	4.4	72.4
HAT/AN/BCN5	23.1	–	–	–	8.8	68.1
HAT/AN/BCN7.5	23.0	–	–	–	13.2	63.8
HAT/AN/BCN10	22.9	–	–	–	17.6	59.5
HAT/Sr $(NO_3)_2$	36.5	–	–	63.5	–	–

of 130°C. Then, since the sample which contained copper nitrate (Cu $(NO_3)_2$), calcium nitrate (Ca $(NO_3)_2$), or strontium nitrate (Sr $(NO_3)_2$) caused none of melting, these metal nitrates were adopted as the additives for combustion experiments and thermal analyses. The uniform double salts of compound oxidizer samples were obtained by drying the aqueous solutions of metal nitrate additives and AN.

2.1.1 Gas generating agents for the 52ml deflagration test

The compositions of AN and each metal nitrate at a molar ratio of 6 : 1 were prepared, and they were dealt with as the oxidizer samples. As the gas generating agents for the 52ml deflagration test, composite samples, which were prepared by mixing of oxidizer samples described above with HAT, which is gas generating fuel already put in practical use, at a rate of the oxygen balance (O. B.)=0, were used. And, gas generating agents consist of HAT, AN, and BCN were also prepared. The O. B. of these mixtures were controlled into zero and the ratio of copper of these mixtures were adjusted into 2.5, 5, 7.5, 10 wt. %. Moreover, the mixture of HAT and Sr $(NO_3)_2$ at O. B.=0 was also examined as reference of the system put in practical use.

1.5 g of each mixed components were molded and pressed into 15 pieces of pellets, which has diameter of 7.15 mm. The formulations are shown in Table1.

As the ignition charge, 100mg of powdered composition of flake titanium and potassium nitrate (Ti/KNO_3) was used as a primary ignition charge, and a 250mg pellet of compound of boron and potassium nitrate (B/KNO_3) was used as a secondary ignition charge.

2.1.2 Oxidizers for Phase Stabilization

As the samples for phase condition measurements, the double salt oxidizers, which changed the mixing ratio of a metal nitrate and AN variously, were used. The molar mixing ratio is shown in Table2.

Table 2 The molar mixing ratio of compound oxidizers.

sample	Metal nitrates			AN
	Cu $(NO_3)_2$	Ca $(NO_3)_2$	Sr $(NO_3)_2$	
#1	1			3
#2	1			4
#3	1			5
#4	1			6
#5	1			7
#6	1			9
#7		1		4
#8		1		5
#9		1		6
#10			1	3
#11			1	6

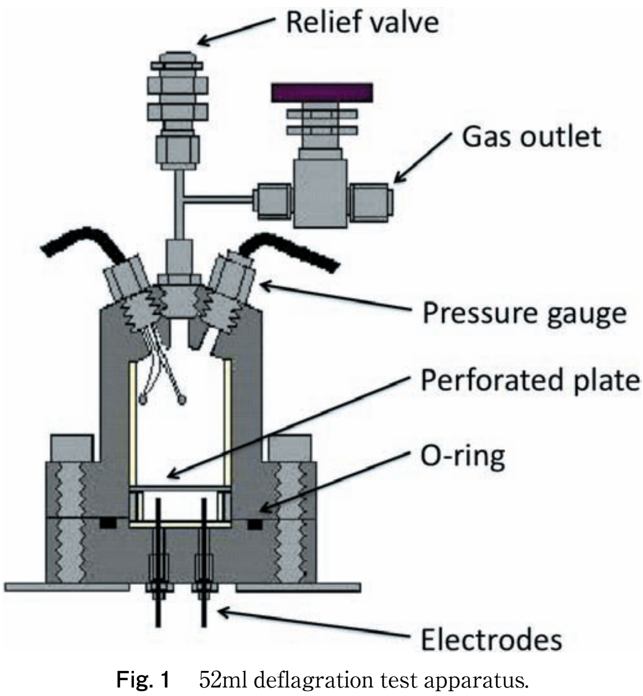

Fig. 1 52ml deflagration test apparatus.

2.2 The 52ml deflagration test

The combustion characteristics were investigated by the pressure profiles (P−t curve), which were measured by the 52ml deflagration test. Fig. 1 is the cross section of the 52ml deflagration test apparatus. The electrodes and ignition charge ignited samples. The pressure transducer measured pressure profiles by the generating gasses. Then, pressure signals were amplified and recorded by the digital oscilloscope. As indexes for combustion characteristics, the maximum pressure (P_{max}) and the maximum pressure rising rate $(dP/dt)_{max}$, which were obtained from

P−t curves were used for evaluation[1].

2.3 SC–DSC

The phase stabilization of AN was investigated by sealed cell differential scanning calorimetry (SC−DSC). Three endothermic peaks (at 50.8°C, 84.1°C, and 125.8°C) of AN's phase transition (between solid phases) temperature were observed and evaluated.

2.4 Calculation of activation energy

Activation energy of exothermic decomposition of the samples was calculated by the Ozawa method. In Ozawa method, the relation of heating rate, exothermic peak temperature, and activation energy is expressed with an Equation (1)[2].

$$E_s = 2.19R[d \log \Phi / d(1/Tm)] \quad (1)$$

E_s : activation energy at combustion surface [J/mol]
Φ : heating rate [K/min]
T_m : exothermic peak temperature [K]
R : gas constant

Equation (1)can be changed as following Equation (2).

$$\log \Phi = -0.457 E_s / R(1/T_m) + \text{constant} \quad (2)$$

Then, since the straight line obtained from the Arrhenius plot of the log of heating rate to reciprocal of exothermic peak temperature has slope of −0.457 Es/R, activation energy can be calculated.

3. Results and discussion

3.1 Combustion characteristics

3.1.1 Pressure profile of gas generating agents

The time−pressure curves obtained by the 52ml deflagration test are shown in Fig. 2. The values of pressure, the times to reach to P_{max}, and $(dP/dt)_{max}$ are shown in Table3.

About samples using double salt oxidizers, although the quantity of HAT was almost the same in the mixture and AN in oxidaizer was decreasing, the values of $(dP/dt)_{max}$ were large, and the times to arrive to $(dP/dt)_{max}$ were short for the samples using the double salt oxidizers comparing with the system of HAT/AN. It turned out that P_{max} increased by 1.2 to 1.5 times, and $(dP/dt)_{max}$ increased by 1.3 to 5.1 times by addition of metal nitrates comparing to HAT/AN. Thereby, the improvement effects in combustion characteristics over HAT/AN mixture by processing AN into double salts with metal nitrates were clarified. And, compared by the values of $(dP/dt)_{max}$, the effect was large in the order of Cu $(NO_3)_2$, >Ca $(NO_3)_2$, >Sr $(NO_3)_2$. Moreover, the improvement effect in combustion characteristics by addition of Cu $(NO_3)_2$ was especially remarkable, and the combustion characteristics was superior to that of HAT/ Sr $(NO_3)_2$, which is put in practical use.

On the ther hand, from the pressure profile of HAT/AN /BCN mixtures, it was suggesuted that the addition of

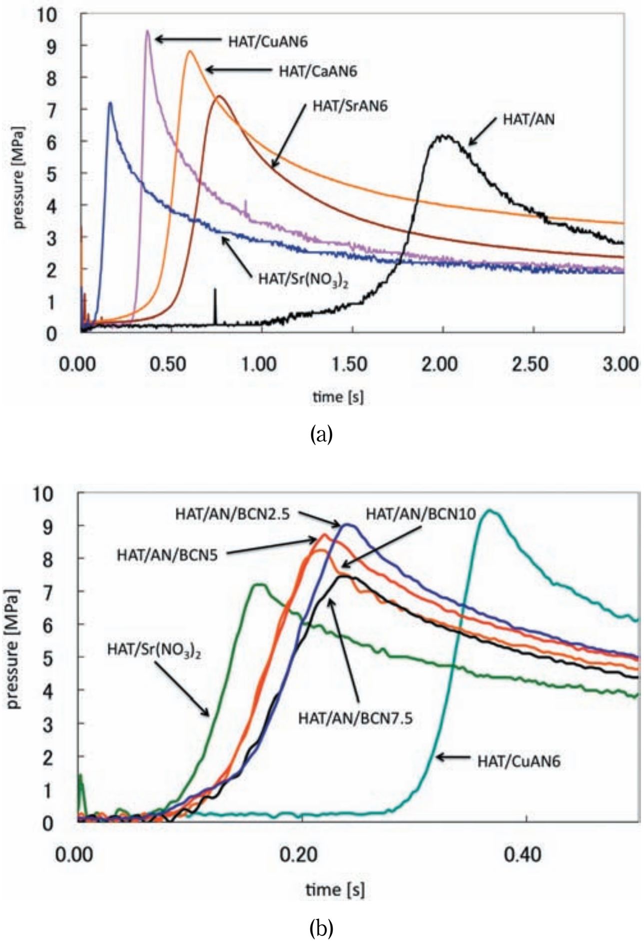

Fig. 2 pressure profile of 52ml deflagration tests
(a) HAT and AN/metal nitrate double salts mixtures
(b) HAT, AN, BCN mixtures.

Table 3 The values of P_{max}, $(dP/dt)_{max}$ and the times to reach to P_{max}, $(dP/dt)_{max}$.

sample	Pmax	Time to Pmax	(dP/dt)max	Time to (dP/dt)max	Cu content
	[MPa]	[s]	[MPa/s]	[s]	[wt.%]
HAT/AN	6.2	1.99	37.5	1.89	
HAT/CuAN6	9.5	0.37	190.0	0.34	6.0
HAT/CaAN6	8.8	0.60	66.1	0.53	
HAT/SrAN6	7.4	0.77	47.9	0.67	
HAT/Sr $(NO_3)_2$	7.2	0.16	143.1	0.14	
HAT/AN/BCN2.5	9.0		122.5		2.5
HAT/AN/BCN5	8.7		104.9		5.0
HAT/AN/BCN7.5	7.5		97.6		7.5
HAT/AN/BCN10	8.2		133.3		10.0

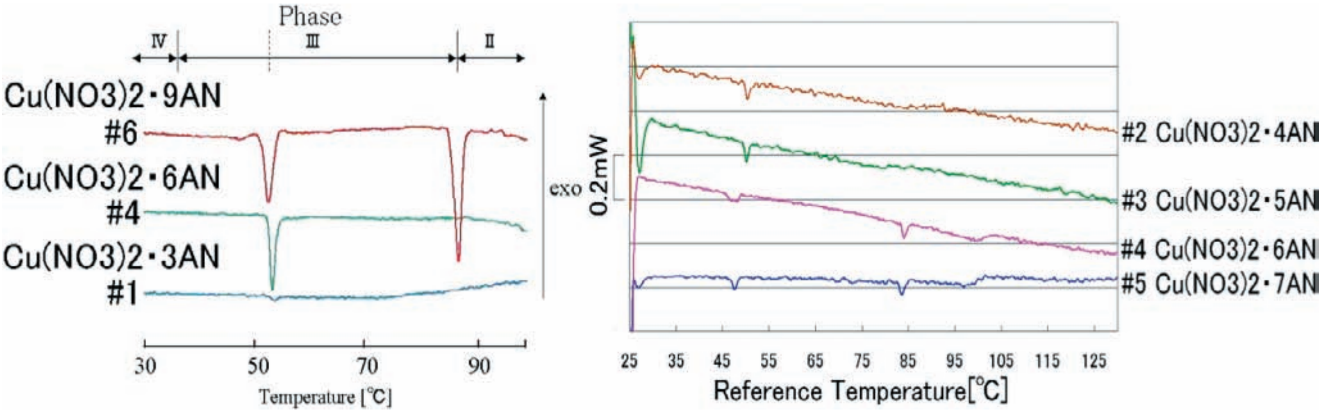

Fig. 3 DSC traces of Cu $(NO_3)_2$/AN mixtures.

Table 4 Activation energy of Ca $(NO_3)_2$/AN compound oxidizer and AN.

Oxidizer	Activation Energy [kJ/mol]
CaAN6	125.9
NH4NO3	120.9

BCN to HAT/AN is effective to enhance the combustion characteristics, but quantitative effect was not shown, for the measured values of P_{max} and $(dP/dt)_{max}$ seem not to have correlation with the amount of added BCN.

3.1.2 Activation energy of Ca $(NO_3)_2$/AN compound oxidizer and AN

The Equation (3) shows the burning rate of gas generating agent[3].

$$r = Z_s \exp(-E_s/RT_s) \qquad (3)$$

r : burning rate [m/s]
E_s : activation energy at combustion surface [J/mol]
T_s : temperature of combustion surface [K]
Z_s : coefficient factor
R : gas constant

From this equation, the rise of $[T_s]$ or reduction of $[E_s]$ is required in order to increase the burning rate [r] of the compositions. So, activation energy $[E_s]$ was calculated by the Ozawa method, and the mechanism of improvement in combustion characteristics was considered. Table4 is the results of activation energy calculation.

There was no big difference between the values of apparent activation energy per mole of Ca $(NO_3)_2$/AN compound oxidizer and AN. So, addition of Ca $(NO_3)_2$ into AN does not affect on thermal decomposition of AN. About improvement in combustion property by the addition of Ca $(NO_3)_2$ to HAT/AN, it can be thought that Ca $(NO_3)_2$ affects catalytically at gas phase combustion reaction of HAT/AN.

3.2 Phase stabilization of AN by addition of metal nitrates

3.2.1 Effect of Cu $(NO_3)_2$

The results of SC-DSC measurements of the compound oxidizers, which contained Cu $(NO_3)_2$ and AN, are shown in Fig. 3.

From the results, it was turned out that endothermic behavior at 125.8°C among three endothermic behaviors which AN shows was stabilized by1 : 7mixtures of Cu $(NO_3)_2$/AN, that one at 84.1°C was stabilized by the mixture ratio of1 : 6, and that phase transitions were stabilized completely by the mixture ratio of1 : 3.

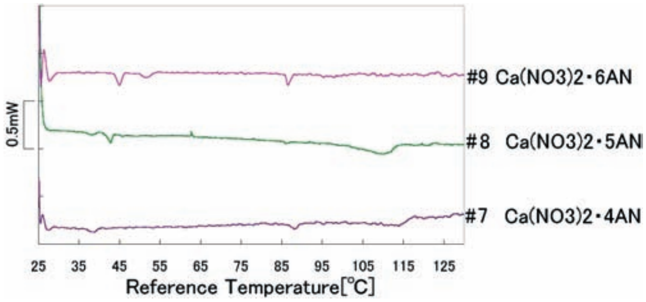

Fig. 4 DSC traces of Ca $(NO_3)_2$/AN mixtures.

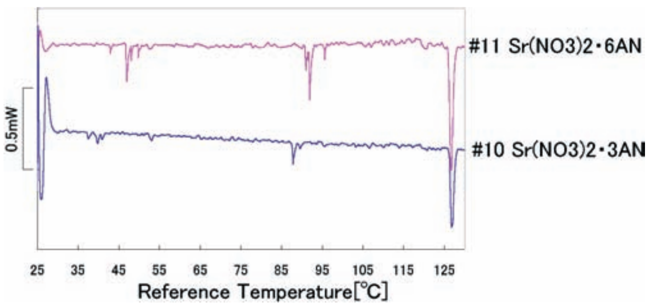

Fig. 5 DSC traces of Sr $(NO_3)_2$/AN mixtures.

3.2.2 Effect of Ca $(NO_3)_2$

The results of SC-DSC measurements of the compound oxidizers, which contained Ca $(NO_3)_2$ and AN, are shown in Fig. 4.

From the results, it turned out that endothermic behavior at 125.8°C was stabilized by1 : 6 mixtures of Ca $(NO_3)_2$/AN, and that phase transitions were stabilized completely by the mixture ratio of 1 : 4.

3.2.3 Effect of Sr $(NO_3)_2$

The results of SC-DSC measurements of the compound oxidizers, which contained Sr $(NO_3)_2$ and AN, are shown in Fig. 5.

Table 5 The theoretical amount of residual substance generation

Sample	Amount of residual substance generation (wt.%)
HAT/AN	0.0
HAT/CuAN6	7.6
HAT/CaAN6	6.2
HAT/SrAN6	10.8
HAT/Sr $(NO_3)_2$	31.1

Sr $(NO_3)_2$/AN did not show sufficient phase stabilization effect even if for the mixture ratio of1 : 3.

3.3 The theoretical rate of residual substance generation

The theoretical rate of residual substance generation of the samples is shown in Table5. The production rates of residual substances from the samples using compound oxidizers were about 10 wt.%. And, these values are about one-third of the production rate of residual substances from HAT/ Sr $(NO_3)_2$, which is put in practical use. So, it was suggested that using compound oxidizers, which consist of AN and metal nitrate, instead of using Sr $(NO_3)_2$ oxidizer, is highly effective to reduce the production of residual substances from gas generating agents.

4. Conclusion

In order to apply AN as an oxidizer of the gas generating agent for airbags, improvement in the combustion characteristics and the phase stability of AN was tried, by using compound oxidizers, in which metal nitrate was added to AN.

When Cu $(NO_3)_2$ was added, this effect was remarkably high, and the oxidizer complex was superior to the conventional system which used HAT/ Sr $(NO_3)_2$. So, Cu $(NO_3)_2$/AN compound oxidizer can be expected as new oxidizer composition which reduced the amount of residual substances.

As the results of SC-DSC measurement about the oxidizers which were prepared to add Cu $(NO_3)_2$, Ca$(NO_3)_2$, and Sr $(NO_3)_2$ to AN, the phase stabilization effect can be obtained for AN with Cu $(NO_3)_2$ and Ca $(NO_3)_2$.

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ガス発生剤酸化剤としての硝酸アンモニウム —金属硝酸塩複塩に関する研究

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自動車用エアバッグガス発生剤の新規酸化剤候補として硝酸アンモニウム（以下ANと略記）の実用化を目指し，５－amino－１－H-tatrazole（以下HATと略記），およびANからなるガス発生剤の燃焼並びに熱分解挙動が検討された。ANを硝酸銅，あるいは硝酸カルシウムを用いて複塩化して用いる事により，HAT/ANガス発生剤の燃焼特性が改善される事が示唆された。また，HAT,AN，塩基性硝酸銅（以下BCNと略記）からなるモデルガス発生剤についても燃焼特性を検討し，BCNの添加がHAT/ANガス発生剤の燃焼成向上に有効である事が示唆された。

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