Study on new gas-generating agents (I)
A small scale deflagration test for evaluation of deflagration properties for tetrazole-oxidizer compositions

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In order to obtain some information on the deflagration properties of new gas-generating agents for airbag systems, we have attemped to devise a small scale deflagration test method, and have investigated its applicability as a screening test to the evaluation of the deflagration properties for new gas-generating agents by examining the influence of testing conditions on the deflagration properties and comparing their data with those obtained from the 1 L tank test method, a good test method for examining the deflagration properties of gas-generating agents for airbag systems.

As the results, we can say that the small scale deflagration test method devised should be useful as a screening test for evaluating the deflagration properties of new gas-generating agents.

1. Introduction

Airbag systems are well known to be a useful tool for protecting lives in the car crash accidents. Sodium azide is now chiefly used as a base material for the gas-generating agents of airbag systems. However, as sodium azide has not only strong toxicity but also possibility for the formation of explosive materials from its reaction with heavy metals, many researches have been carried out to find out new gas-generating agents.

The pressure release behavior of gas generating agents by thermal decomposition has already been reported by authors[1,2,3,4]. However, the screening test for evaluating the deflagration properties of gas-generating agents has not been established. Therefore, we devised a small scale deflagration test apparatus and investigated its applicability to preliminary evaluation by examining the influence of testing conditions on the deflagration properties and comparing their data on the deflagration properties with those obtained from the 1 L tank test[5], which is well known to be a good but larger scale test for evaluating the deflagration properties of gas-generating agents for airbag systems.

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2. Experimental

2.1 Materials

2.1.1 Tetrazoles and oxidizers

Tetrazoles used in the experiments are shown in Table 1. HAT was purchased from Toyo Kasei Co., Ltd.. Other tetrazoles were kindly supplied from Tokyo Kasei Co., Ltd.. KNO_3 and $KClO_4$ are of special grade and were purchased from Wako Pure Chemical Industries, Ltd.. Tetrazoles and oxidizers were used without further purification.

Tetrazole-oxidizer powder compositions were propared by mixing a tetrazole and an oxidizer in the V-type mixer or by mixing them with a brush. AS-

Table 1 Tetrazole used (abbreviation and purity)

Tetrazoles	Abbreviation	Purity (wt. %)
5-Amino-1H-tetrazole	HAT	>98.0
Disodium 1H-tetrazole-5-carboxylic acid	TCA	97.2
Dipotassium bitetrazole	BHTK	99.5

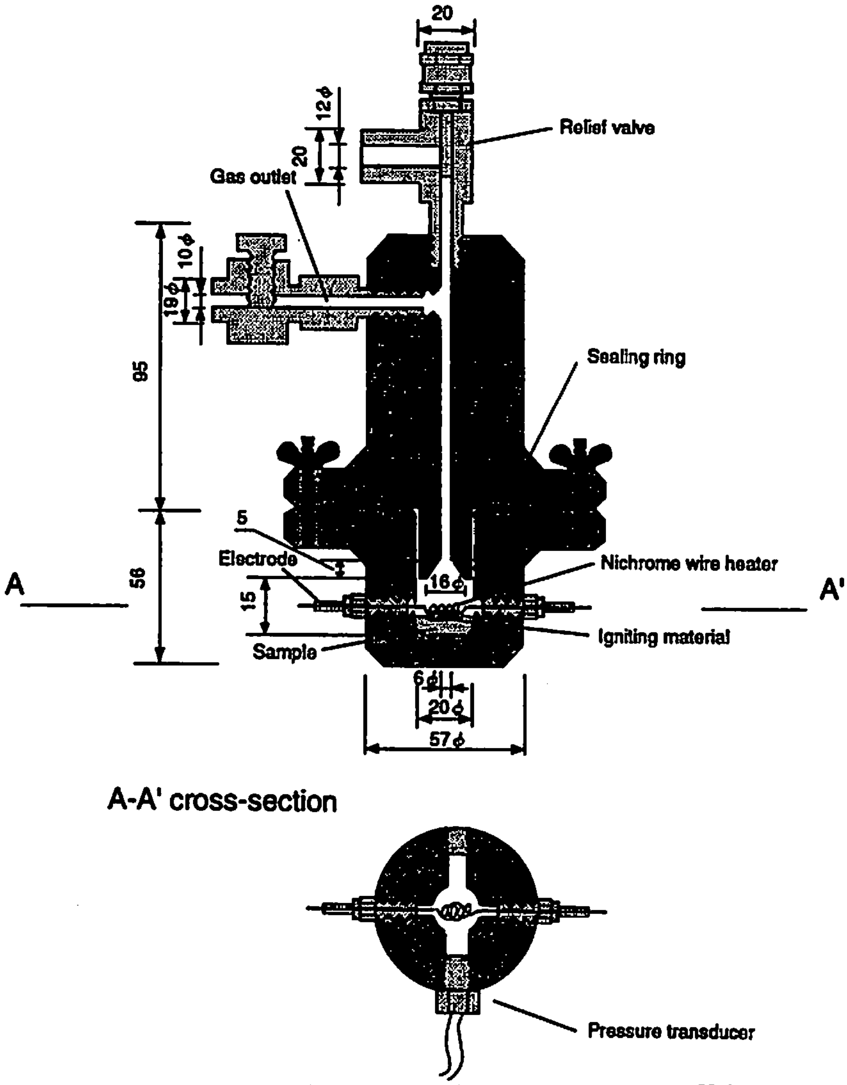

Fig. 1 Cross-section of small scale deflagration test apparatus (Unit: mm)

82 is a commercial sodium azide type of gas-generating agent and its powder composition and pellet were supplied from Nippon Kayaku Co., Ltd.

2.1.2 Igniting material

Pb_3O_4 and Si are of reagent grade and were purchased from Wako Pure Chemical Industries, Ltd.. An igniting material was prepared by mixing Pb_3O_4 (70wt.%) and Si (30wt.%) carefully with a brush.

2.2 Apparatus

Fig. 1 shows a cross-section of a small scale

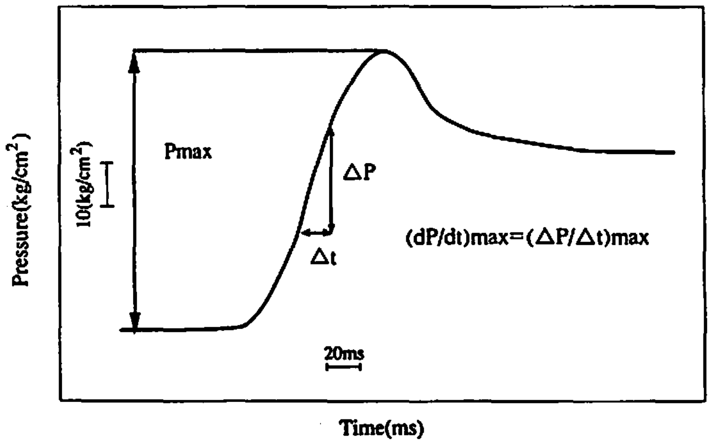

Fig. 2 Typical time-pressure curve in the deflagration of the BHTK-KNO_3 composition
Sample: 6 φ pellet of BHTK(51.5wt.%) - KNO_3 (48.5wt.%) composition, 0.5 g
Igniter: 0.2 g

deflagration test apparatus. The apparatus consists of a cylindrical closed vessel (ca. 13㎤ capacity) made of stainless steel fitted with electrodes to which a nichrome wire (0.2㎜ diameter, 80㎜ length) as a heater is attached to fire an igniting material by an exploder (30V) and connected to a pressure recording system. An adjustable relief valve vents gas to the atmosphere at a desirable pressure from 750 to 1500 psi (5.2 - 10.5MPa) to protect the apparatus from explosion. The pressure developed in the chamber by the deflagration of the gas-generating agent is detected with a transducer (Type E501 from Kyowa Electronic Instrument Co., Ltd.) in the tubular lower arm (6㎜ internal diameter, 34㎜ length), is amplified by a charge amplifier (Type DMP-611A from Kyowa Electronic Instrument Co., Ltd.) and is recorded on a digital memory (Type DS-8613 from Iwatsu Co., Ltd.).

2.3 Test procedure

0.5 g of a sample is introduced in the chamber and 0.1−0.4 g of the igniting material is then placed on it so as to be in sufficient contact with the nichrome wire heater. The vessel is closed and the firing leads are connected to the terminals of the electrodes. The sample is then ignited by operating the dynamo at a remote place. Time-pressure profiles by the deflagration of gas-generating agents in the chamber are measured.

3. Results and Discussion

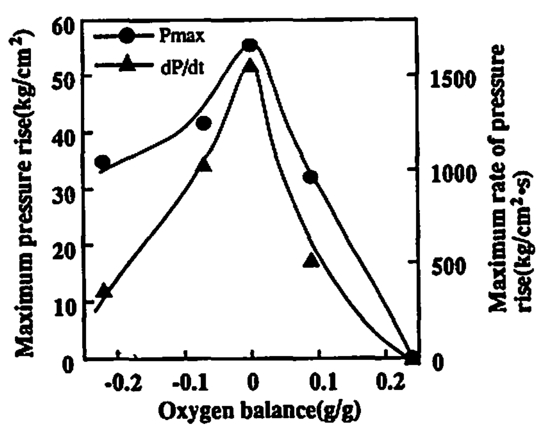

Fig. 3 Plots of maximum pressure rise and maximum rate of pressure rise against oxygen balance in the deflagration of the BHTK-KNO_3 composition
Sample: 6 φ pellet of BHTK-KNO_3 composition, 0.5 g
Igniter: 0.2 g

3.1 Time-pressure curve

Fig. 2 shows a typical time-pressure curve in the deflagration of the BHTK(51.5wt.%) - KNO_3 (48.5wt.%) composition. As shown in Fig. 2, we can obtain the maximum pressure rise and the maximum rate of pressure rise from the time-pressure curve, which are important deflagration properties.

3.2 Effects of test conditions on deflagration properties

3.2.1 Effects of oxygen balance

Fig. 3 shows changes of the maximum pressure

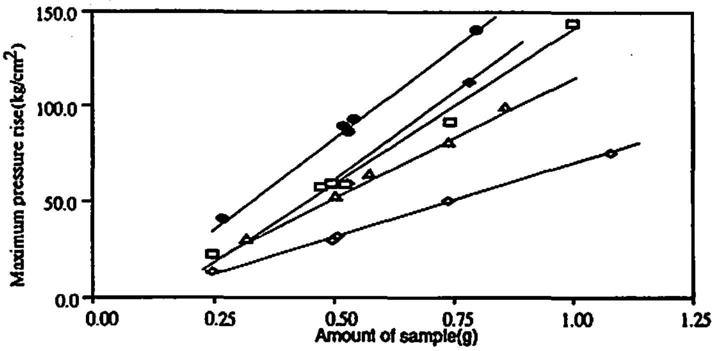

Fig. 4 Plots of maximum pressure rise against amount of sample in the deflagration of the tetrazole-oxidizer composition
Sample: 6 ϕ pellet of the tetrazole-oxidizer composition
Igniter: 0.2 g

	Tetrazole (wt. %)	Oxidizer (wt. %)
△ AS−82		
⊕ $HAT/KClO_4$	41.3	58.7
◆ HAT/KNO_3	37.5	62.5
◇ TCA/KNO_3	56.6	43.4
□ $BHTK/KNO_3$	51.5	48.5

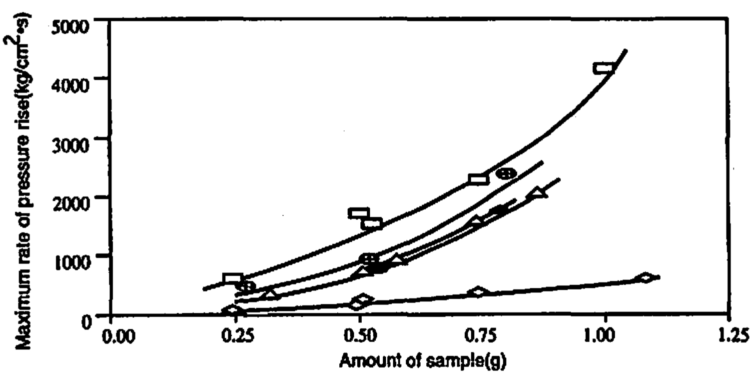

Fig. 5 Plots of maximum rate of pressure rise against amount of sample in the deflagration of the tetrazole-oxidizer composition
Sample: 6 ϕ pellet of the tetrazole-oxidizer composition
Igniter: 0.2 g

	Tetrazole (wt. %)	Oxidizer (wt. %)
△ AS−82		
⊕ $HAT/KClO_4$	41.3	58.7
◆ HAT/KNO_3	37.5	62.5
◇ TCA/KNO_3	56.6	43.4
□ $BHTK/KNO_3$	51.5	48.5

rise and the maximum rate of pressure rise by deflagration with oxygen balance of the $BHTK-KNO_3$ compositions.

From Fig. 3, we can say that the maximum pressure rise and the maximum rate of pressure rise by deflagration should give their maximum values at the composition giving zero oxygen balance.

Consequently we used the tetrazole-oxidizer composition at zero oxygen balance for the standard test hereafter

3.2.2 Amount of sample

Fig. 4 and Fig. 5 show the effects of the amount of a sample on the maximum pressure rise and the maximum rate of pressure rise in the deflagration of the tetrazole-oxidizer compositions.

As shown in Fig. 4 and Fig. 5, the maximum pressure rise is linear against the amount of a sample but the maximum rate of pressure rise has a tendency to increase in a nearly exponential manner with an increase in the amount of a sample, suggesting the effects of pressure on the rate of pressure rise.

In our research, chiefly we used 0.5 g of the sample for the standard test.

3.2.3 Amount of igniting material

Fig. 6 shows the effects of the amount of the igniting material on the maximum pressure rise and the maximum rate of pressure rise in the deflagration of the BHTK(51.5wt.%) - KNO_3 (48.5wt.%) composition. As shown in Fig. 6, we can say that the amount of the igniting material has no remarkable effects on the deflagration properties of the tetrazole-oxidizer compositions.

Consequently we used 0.2 g of the igniting material for the standard test hereafter.

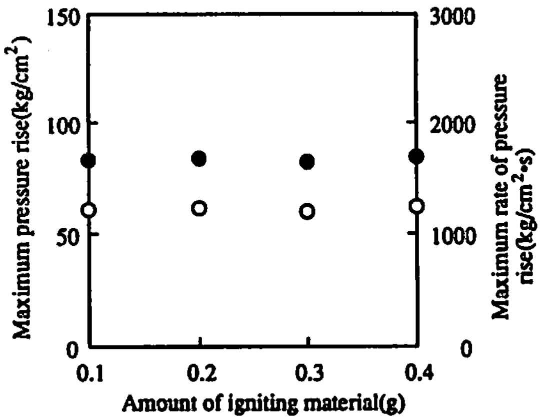

Fig. 6 Effects of amount of igniting material on maximum pressure rise and maximum rate of pressure rise in the deflagration of BHTK-KNO_3 composition
Sample: 10φ pellet of BHTK(51.5wt.%) - KNO_3 (48.5wt.%) 0.5 g
○ Maximum pressure rise
● Maximum rate of pressure rise

3.2.4 Charge density and surface area of sample

Table 2 shows the effects of surface areas of BHTK and KNO_3 powder samples on the deflagration properties.

From Table 2, we can say that the surface areas of a tetrazole and an oxidizer have remarkable effects on the maximum rate of pressure rise.

Fig. 7 shows the effects of the surface areas of the pellets of BHTK(51.5wt.%) and KNO_3 (48.5wt.%) composition on the deflagration properties.

From Fig. 7 we can say that the maximum rate of pressure rise by deflagration has a remarkable tendency to increase linearly with an increase in the surface areas of the pellets.

Fig. 8 shows the effects of the charge density of the sample on the deflagration properties. As shown in Fig. 8, the maximum pressure rise and especially the maximum rate of pressure rise have a remarkable tendency to decrease linearly with an increase in the charge density of the sample.

From the above results, the effects of surface areas of a tetrazole and an oxidizer and the effects of surface area of the composition and the charge density of the composition on the rate of pressure rise suggest that at least the deflagration rates should depend on the surface areas of a tetrazole and an oxidizer and the surface area of their composition.

3.3 Applicability for the screening test

Fig. 9 and Fig. 10 show the comparison of the deflagration properties obtained from the small scale

Table 2 Effects of particle size of BHTK and KNO_3 on maximum pressure rise and maximum rate of pressure rise in the deflagration of the BHTK-KNO_3 composition
Sample: BHTK(51.5wt.%) - KNO_3 (48.5wt.%), 0.5 g
Igniter: 0.2 g

Granularity of BHTK (mesh)	Granularity of KNO_3 (mesh)	Pmax (kg/cm²)	(dP/dt)max (kg/cm²·s)
100～200	100～200	42.3	552
200～300	200～300	50.3	1644
>300	>300	53.3	2125

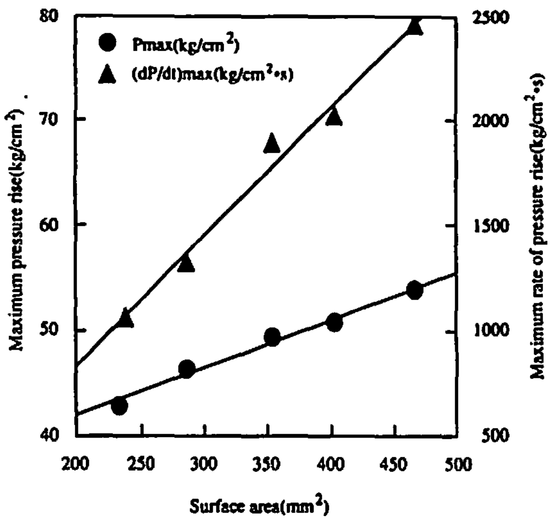

Fig. 7 Plots of maximum pressure rise and maximum rate of pressure rise against surface areas of pellets in the deflagration of the BHTK−KNO_3 composition

Sample: 6 mmϕ pellet of BHTK(51.5wt.%) −KNO_3 (48.5wt.%) composition,0.5 g

Pellet height(mm)	Weight(g)	Surface area(㎠)
0.97	0.05	75
1.95	0.10	93
2.81	0.15	110
3.90	0.20	130
4.66	0.25	114
9.66	0.50	237

Igniter:0.2 g

deflagration test with those obtained from the 1 L tank test[5], which is a good and larger scale test to evaluate the deflagration properties of gas-generating agents for airbag systems. As shown in Fig. 9 and Fig. 10, there are good relationships in the deflagration properties between two tests.

Therefore, we can say that the small scale deflagration test should be a good screening test for evaluating the deflagration properties of the tetrazole-oxidizer compositions.

4. Conclusion

In order to obtain some information on the deflagration properties of new gas-generating agents, we have devised the small scale deflagration test, have examined influences of testing conditions on the deflagration properties and have compared the data obtained from the small scale deflagration test with those obtain from the 1 L tank test, which is known to be a good and larger scale test for the gas-generating agents of airbag systems.

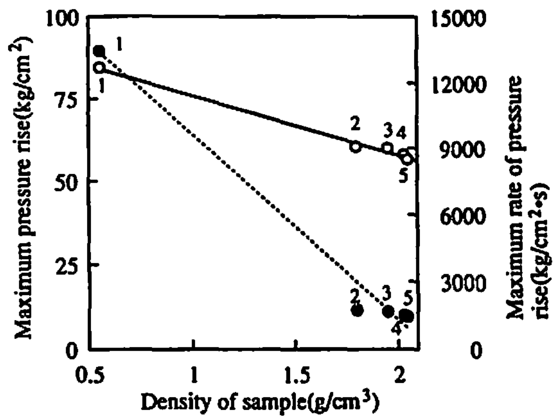

Fig. 8 Plots of maximum pressure rise and maximum rate of pressure rise against density of sample in the deflagration of the BHTK-KNO_3 composition

Sample: 6 mmϕ pellet and powder of BHTK(51.5wt.%) - KNO_3 (48.5wt.%) composition,0.5 g

Igniter:0.2 g

○ Maximum pressure rise

● Maximum rate of pressure rise

1 is powder

2, 3, 4 and 5 is pellet and their moulding pressure is 44.2,88.4,132.6 and 176.8kg/㎠ respectively

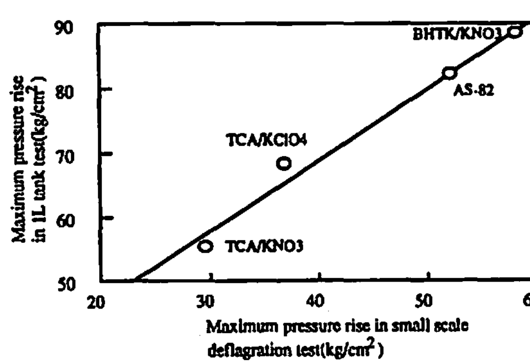

Fig. 9 Relationship in maximum pressure rise between 1 L tank test and small scale deflagration test in the deflagration of the tetrazole-oxidizer compositions

Small scale deflagration test:

Sample: 6ϕ or 10ϕ pellet of the tetrazole -oxidizer composition,0.5 g

Igniter:0.2 g

1 L tank test:

Sample: 6ϕ or 10ϕ pellet of the tetrazole -oxidizer composition,25 g

Igniter:Ignitor(from Nippon Kayaku Co.Ltd.)

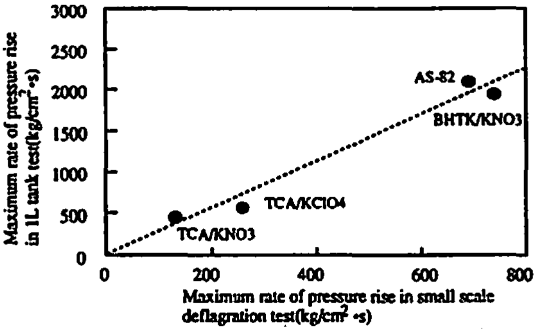

Fig. 10 Relationship in maximum rate of pressure rise between 1 L tank test and small scale deflagration test in the deflagration of the tetrazole-oxidizer compositions
Small scale deflagration test:
Sample: 6 ϕ or 10ϕ pellet of the tetrazole -oxidizer composition, 0.5 g
Igniter: 0.2 g
1 L tank test:
Sample: 6 ϕ or 10ϕ pellet of the tetrazole -oxidizer composition, 25 g
Igniter: Igniter (from Nippon Kayaku Co.Ltd.)

As the results, we can say that the small scale deflagration test should be a useful screening test for evaluating the deflagration properties of new gas-generating agents.

5. Acknowlegement

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新規ガス発生剤に関する研究（I）
テトラゾール組成物の爆燃特性評価のための小型爆燃試験

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田村昌三*

自動車エアバッグ用新規ガス発生剤の爆燃特性を評価するスクリーニング試験法として小型爆燃試験装置を試作し，この装置を利用して，新規ガス発生剤候補組成物の爆燃特性評価への適応性を調べた。その結果，小型爆燃試験による評価結果は現在その有効性がよく知られている1Lタンク試験による評価結果と良い相関関係を持つことが明らかになった。

この結果より，小型爆燃試験はガス発生剤の爆燃特性を評価する有効なスクリーニング試験であると言える。

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