Research paper

Effect of additional copper(II) oxide on the combustion of 5-amino-1H-tetrazole and lithium perchlorate mixtures (I)
— Examination of the burning mechanism —

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Abstract

Recently, 5-amino-1H-tetrazole (5-ATZ) has been developed for practical use as a substitute to sodium azide, which has been used conventionally as a fuel component of gas generating mixtures for automobile airbags. In this study, the combustion of the mixture of 5-ATZ / lithium perchlorate $LiClO_4$ and the effect of additional copper(II) oxide CuO have been examined. $LiClO_4$ is an oxidizer with high oxygen content per unit mass. 5-ATZ / $LiClO_4$ mixture has displayed higher linear burning rate and superior gas generating ability than 5-ATZ / strontium nitrate $Sr(NO_3)_2$ mixture which has been put to practical use. It was found that the granular diffusion flame model was applicable to the samples tested. In addition, it was shown that within the pressure range of 1 - 5 MPa, the rate-determining step of the linear burning rate was the diffusion process. There was an increase in the linear burning rate when a small amount of CuO was added to 5-ATZ / $LiClO_4$ mixture. This is probably because of the shortening of the diffusion distance, which leads to the flame approaching the burning surface and hence to an increase in the amount of heat feedback.

Keywords: 5-Amino-1H-tetrazole, Lithium perchlorate, Copper(II) oxide, Granular diffusion flame model, Gas generating mixtures.

1. Introduction

Performances of gas generating mixtures are determined generally by the combination of the fuel and the oxidizer. The authors have been using 5-amino-1H-tetrazole (5-ATZ), a tetrazole compound which has been utilized as a substitute fuel component to sodium azide for airbag gas generating mixtures, and mixing with various oxidizers, the authors have been investigating on combustion characteristics of mixtures with improved performance, as compared to mixtures which have already been put into practical use. There have been extensive studies [1)-3)] on nitrogen gas generating mixtures that utilize 5-ATZ. The authors have also reported on the combustion characteristics of 5-ATZ-based mixtures that use potassium perchlorate $KClO_4$ [4)], strontium nitrate $Sr(NO_3)_2$ [5)], potassium nitrate KNO_3 [6)] and sodium nitrate $NaNO_3$ [6)], sodium perchlorate $NaClO_4$ [7)] as oxidizers. As for 5-ATZ / KNO_3 mixtures and 5-ATZ / $NaNO_3$ mixtures, it was also found that the burning mechanism can be explained by the granular diffusion flame (GDF) model [8)]. Since lithium atom has a small mass number, its salt is relatively light, hence the mass percentage of the oxidizer per unit mass of the stoichiometric ratio mixture will become small, leading to an estimated increase in the amount of generated gas per unit mass of the mixture. In this study, combustion characteristics of mixtures that contain 5-ATZ as a fuel, lithium perchlorate $LiClO_4$ as an oxidizer, and copper(II) oxide CuO as an additive were examined. Burning mechanism was also examined, demonstrating that the combustion of 5-ATZ / $LiClO_4$ / CuO mixtures could be explained adequately by the GDF model.

2. Experimental

2.1 Materials

As a fuel component of gas generating mixtures, 5-ATZ (Fujimoto Chemicals Co., Ltd., free sample) was used. $LiClO_4$ (Kanto Chemical Co., Inc., Kanto extra pure reagent >97 %) and CuO (Kanto Chemical Co., Inc., JIS special grade reagent >98 %) were used as oxidizers. 5-ATZ and $LiClO_4$ were crushed in separate ball mills

Table 1 Compositions of 5-ATZ/oxidizer mixtures.

Designation		MixA	MixB	MixC	MixD	MixE
5-ATZ (wt%)		47.7	46.4	41.6	23.4	36.5
Oxidizer (wt%)	$LiClO_4$	52.3	49.3	39.0	—	—
	CuO	—	4.3	19.4	76.6	—
	$Sr(NO_3)_2$	—	—	—	—	63.5
Apparent density ($g\ cm^{-3}$)		1.81	1.88	2.01	2.48	2.15
Theoretical maximum density ($g\ cm^{-3}$)		1.88	1.93	2.14	3.61	2.19
Porosity (%)		3.72	2.59	6.07	31.3	1.83
Theoretical amount of generated gas	($\times 10^{-2}$ mol g^{-1})	2.81	2.73	2.44	1.38	2.44
	($\times 10^{-2}$ mol cm^{-3})	5.26	5.25	5.22	4.96	5.36
Adiabatic flame temperature (K)		3101	3031	2718	1782	2788

(Irieshokai Co., Ltd., V-2, 100 r.p.m, 900 ml pot, 15 mm diameter porcelain balls) for approx. one hour, and particle diameters were controlled within 75 – 149 μm by using standard sieves. In order to examine the effect of CuO addition, 4.3 wt % (5.13 mol %) and 19.4 wt % (22.2 mol %) of CuO were added to 5-ATZ / $LiClO_4$ mixtures. The samples were then dried by using vacuum dryer (Kuramotikagaku Co., Ltd., RG-501) at chamber temperature of 328 K and at pressure of 10 Pa for four hours, and they were mixed at stoichiometric ratio for 30 minutes at 80r.p.m. through a rotary mixer (Tsutsui Scientific Instruments Co., Ltd., S-3). Sample of approx. four grams was pressed into a strand whose dimension was approx. 5 × 5 × 70 mm, by using a hydraulic press in which approx. 0.6 GPa was exerted for 5 min. All parts of the surface of a strand except for the top surface were applied with epoxy resin. Apparent density was derived by measuring the mass and the dimension of a strand before the application of restrictor. Table 1 gives the mixing ratio and the porosity of each sample mixed at stoichiometric ratio.

2.2 Measurement of linear burning rate

The testing procedures are described elsewhere[6), 7)].

2.3 Measurement of pressure and temperature within the closed vessel

In order to acquire fundamental data of performances of gas generating mixtures, the 60 liter tank test is conducted in general[9)], measuring the pressure-time history for each candidate material. In this study, a chimney-type strand burner (Kyowagiken Co., Ltd., SCTA-50), which is generally used for the measurement of linear burning rate *r*, was confined to act as a four-liter closed vessel, and pressure-time change was measured at an initial N_2 operational pressure of 2 MPa[10), 11)]. Temperature within the vessel was measured by using K-type (alumel-chromel) thermocouple which was installed at the upper part of the burner, and the result was recorded on a pen recorder (Rikadenki Co., Ltd., R-64).

3. Results and discussion

3.1 Linear burning rate

In general, gas generating mixtures with higher burning rate is preferable. Even with the mixtures of low burning rate, it is possible to generate large amount of gas within a short period of time if the pellets are small. However, since it is difficult to manufacture extremely small pellets, the mixtures with faster burning rate are better.

The relationship between *r* and *P*, which is known as Vielle's law, can be expressed as the next equation (1).

$$r = a P^{n} \qquad (1)$$

Here, *a* is a constant and *n* is a pressure exponent. Figure 1 gives the relationship between *r* and *P* . There were increases in *r* with increases in *P*, obeying Vielle's law for all mixtures. Comparing 5-ATZ / $LiClO_4$ mixture (MixA) with 5-ATZ / $Sr(NO_3)_2$ mixture (MixE), *r* of the former mixture was approximately as twice as fast as the latter.

Since pressure gradient generally increases with an increase in *r*, experiments were conducted in this study in order to examine the effects of CuO addition, which have been found to enhance *r* according to preliminary experiments. As shown in Fig. 1, *r* of MixA has increased with the addition of 4.3 wt% CuO (MixB), but the extent of enhancement was less obvious when 19.4 wt% of CuO was added (MixC), and below 2 MPa, *r* has decreased instead. This is probably because of the low *r* for 5-ATZ / CuO mixture surpassing the reaction enhancement effect through CuO addition. Reaction was enhanced by the addition of CuO probably because CuO may have lowered the temperature of reaction initiation.

3.2 Amount of generated gas

Gas generating mixtures for automobile airbags are required to release large amount of gas with a small amount of sample in order to downsize the inflator.

Oxygen balances for samples used in this experiment are all zero, since theoretically, all of carbon and hydrogen atoms contained in the fuel are assumed to oxidize completely according to the following equations.

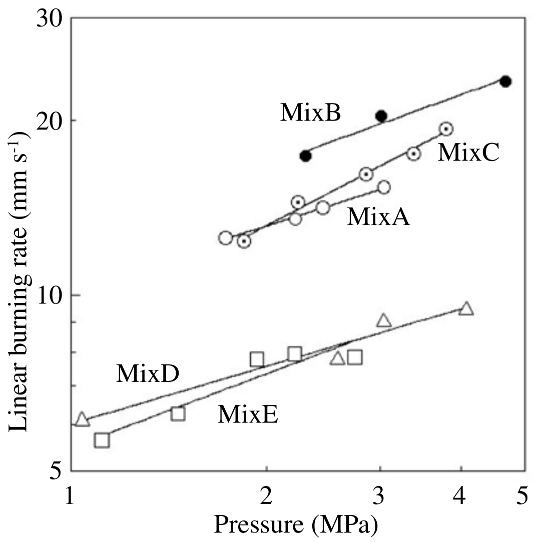

Fig. 1 Linear burning rate of 5-ATZ / oxidizer mixtures.

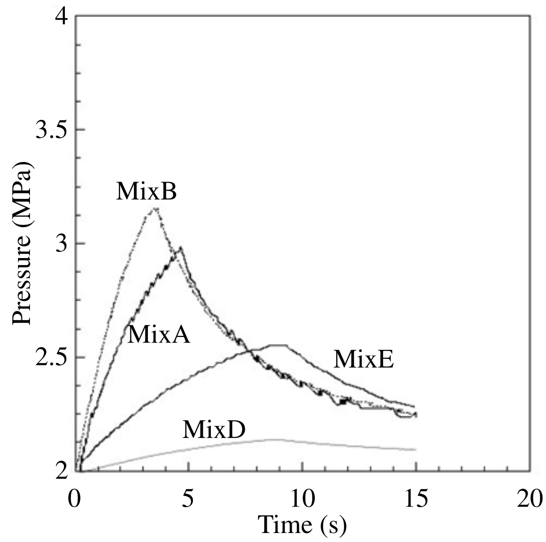

Fig. 2 Pressure-time history of 5-ATZ / oxidizer mixtures from closed vessel test.

In the case of 5-ATZ / $LiClO_4$ mixture:

$$CH_3N_5 + 0.875\ LiClO_4 \rightarrow CO_2 + 1.5\ H_2O + 2.5\ N_2 + 0.875\ LiCl \quad (2)$$

In the case of 5-ATZ / CuO mixture:

$$CH_3N_5 + 3.5\ CuO \rightarrow CO_2 + 1.5\ H_2O + 2.5\ N_2 + 3.5\ Cu \quad (3)$$

In the case of CuO 4.3 wt% addition:

$$CH_3N_5 + 0.85\ LiClO_4 + 0.1\ CuO \rightarrow CO_2 + 1.5\ H_2O + 2.5\ N_2 + 0.85\ LiCl + 0.1\ Cu \quad (4)$$

In the case of CuO 19.4 wt% addition:

$$CH_3N_5 + 0.75\ LiClO_4 + 0.5\ CuO \rightarrow CO_2 + 1.5\ H_2O + 2.5\ N_2 + 0.75\ LiCl + 0.5\ Cu \quad (5)$$

Table 1 gives the calculated values of the amount of generated gas per unit mass and the amount of generated gas per unit volume. If the amount of generated gas per unit mass is large, it is possible to reduce the mass of an inflator. On the other hand, if the amount of generated gas per unit volume of sample is large, it is possible to reduce the volume of the sample necessary to generate equal volume of gas and therefore downsize the inflator. According to Table 1, the amount of generated gas per unit mass of MixA was larger than that of MixE, but it is apparent that the amount of generated gas per unit volume for MixA was inferior to that of MixE.

3.3 Adiabatic flame temperature

Calculated value of adiabatic flame temperature T_f employing chemical equilibrium calculation [12] is given in Table 1. As given in Fig. 1, one of the main reasons for r of MixA being larger than that of MixE is that the mixture containing $LiClO_4$ has a higher T_f than the mixture containing $Sr(NO_3)_2$.

The main reason for a decrease in r with an increase in CuO content of the mixture was probably due to an increase in mass percentage of 5-ATZ / CuO mixture, which exhibits relatively low T_f, leading to a decrease in the amount of heat transfer to the burning surface of the sample.

3.4 Pressure within the closed vessel

Gas generating mixtures for automobile airbags are required to generate large amount of gas in order to fill in the volume of the airbag (*e.g.* 60 liter) within a short period of time.

Figure 2 gives the experimental result of the pressure-time curve within the vessel. The larger the pressure gradient, the faster the deployment of the airbag. From the diagram, the pressure gradient was found to be relatively large for MixA as compared to that of MixE. Although the pressure gradient for MixD was extremely small, addition of a small amount of CuO into MixA have resulted in a remarkable increase in the pressure gradient. The pressure gradient was the largest when 4.3 wt% CuO was added. This is probably because of an increase in r, leading to an increase in the rate of gas generation through the addition of CuO.

3.5 Temperature within the closed vessel

In order to estimate gas temperature inside the actual airbag, gas temperature within the vessel was measured. Figure 3 gives the temperature-time curve within the vessel. Temperatures of combustion gases were in the order of MixA> MixB > MixE> MixD. Especially, temperature inside the vessel for the mixture containing $LiClO_4$ was approx. 30K higher than that of the mixture containing $Sr(NO_3)_2$. Meanwhile, the maximum temperature of generated gas within the vessel T_{max} became lower with the addition of CuO probably because T_f of MixD was relatively low. Since it is preferable for the temperature inside the vessel to be as low as possible, addition of CuO was found to give satisfactory effects on gas generating mixtures for airbags.

3.6 Burning mechanism

In this section, the reasons for an increase in r with the addition of CuO into MixA were examined from the standpoint of the effect of CuO addition upon the burning mechanism.

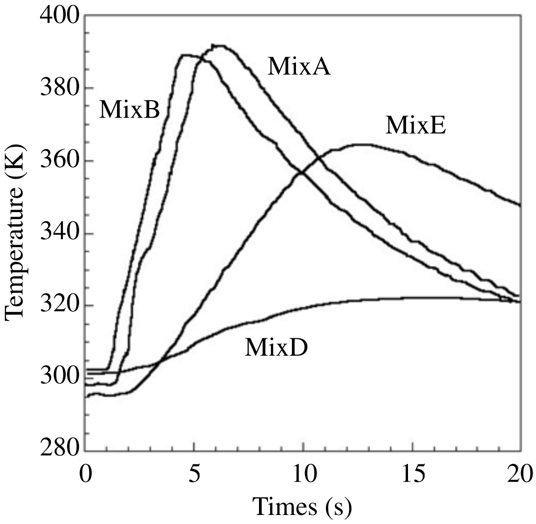

Fig. 3 Temperature-time history of 5-ATZ / oxidizer mixtures from closed vessel test.

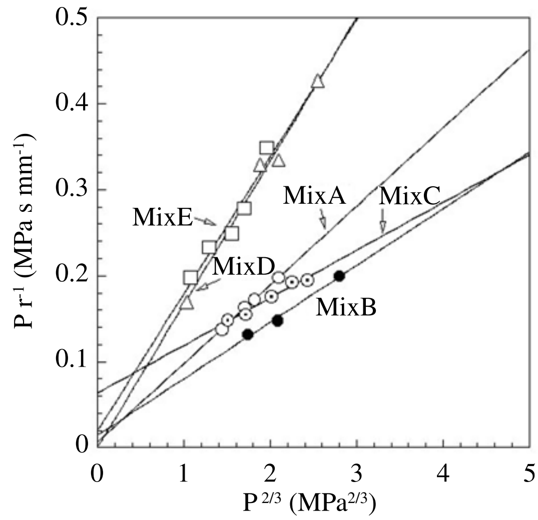

Fig. 4 GDF correlation of linear burning rate with: $(P / r) = a + b\,P^{2/3}$

Table 2 Results of the model $\dfrac{L_d}{L_c} = \dfrac{b}{a}\,P^{2/3}$.

Designation	a	b	b / a	L_d / L_c at 2.0 MPa
MixA	6.90×10^{-3}	9.13×10^{-2}	13.2	21.0
MixB	1.46×10^{-2}	6.58×10^{-2}	4.51	7.15
MixC	6.39×10^{-2}	5.53×10^{-2}	0.865	1.38
MixD	7.00×10^{-4}	1.67×10^{-1}	238	378
MixE	2.02×10^{-2}	1.59×10^{-1}	7.89	12.5

Firstly, whether the GDF model, a combustion model put forward by Summerfield et al. [8], was applicable to samples used in this study was examined through the following equation (6).

$$\frac{1}{r} = \frac{a}{P} + \frac{b}{P^{1/3}} \qquad (6)$$

Here, a is a constant based on the rate of chemical reaction rate in the gas phase, b is a constant based on the rate of diffusion and P is the pressure within the vessel. a and b are both independent to P. Transforming equation (6) gives the following equation (7).

$$\frac{P}{r} = a + bP^{2/3} \qquad (7)$$

Figure 4 shows the relationships between $P^{2/3}$ and P / r for all the mixtures tested. For all the mixtures, good linear relationships were obtained, and since a and b were both positive values, the GDF model was suggested to be applicable for all the mixtures.

Modifying the GDF model, burning rate can be expressed as given in equation (8). Detailed explanations are given in other references [6].

$$\frac{1}{r} = \frac{\rho_s C_s (T_s - T_0 - Q / C_s)(L_c + L_d)}{\lambda_g (T_f - T_s)} \qquad (8)$$

Here, λ_g is the thermal conductivity in the gas phase, ρ_s is the density of the sample, C_s is the specific heat of the sample, T_s is the burning surface temperature, T_0 is the initial temperature, Q is the exothermic heat of decomposition per unit mass of the sample in the condensed phase reaction zone, L_d is the diffusion distance of the fuel component and the oxidizer and L_c is the distance required for chemical reaction. Meanwhile, the ratio between the thickness of the reaction layer and that of the diffusion layer is given in equation (9).

$$\frac{L_d}{L_c} = \frac{b}{a}\,P^{2/3} \qquad (9)$$

When P is greater than 1, the diffusion layer is thought to be thicker than the reaction layer if the right hand side value of equation (9) is greater than l, and if the value is less than l, the reaction layer is suggested to be thicker than the diffusion layer.

Table 2 gives calculated results of L_d / L_c, for all mixtures examined. Since the values of $L_d / L_c = bp^{2/3} / a$ were all greater than 1 at P = 2.0 MPa, the diffusion layer was estimated to be thicker than the reaction layer for each mixture. Therefore, within the pressure range examined in this study, diffusion process was estimated to be the rate determining step of r for each mixture. In addition, examining the calculated values of b / a there was a decrease in the value from 13.2 to 4.51 which led to a decrease in the value of L_d / L_c for MixB, as compared to MixA. This is possibly because of L_d becoming shorter than L_c, or L_c becoming shorter than L_d. However, it is more adequate to

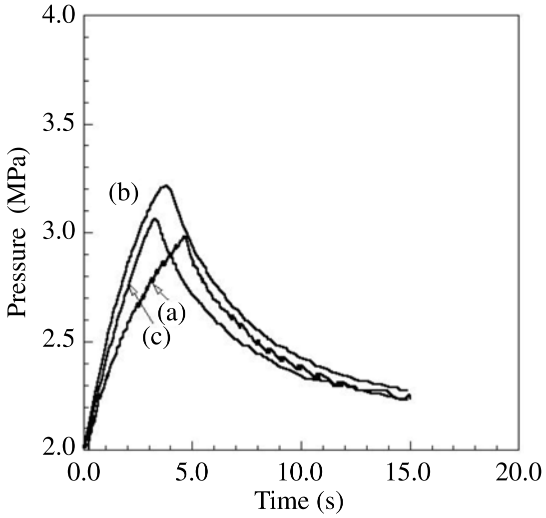

Fig. 5 Effect of the particle size on the pressure-time history of 5-ATZ / $LiClO_4$ mixtures from closed vessel test.
(a) 5-ATZ (75 – 149 μm) / $LiClO_4$ (75 – 149 μm)
(b) 5-ATZ (45 – 74 μm) / $LiClO_4$ (75 – 149 μm)
(c) 5-ATZ (75 – 149 μm) / $LiClO_4$ (45 – 74 μm)

suggest that L_d have become shorter than L_c, because if L_c is longer, temperature gradient becomes smaller, leading to a decrease in the amount of heat transfer from the flame and to a decrease in *r*. Therefore, the reason for an increase in *r* with the addition of CuO into 5-ATZ/$LiClO_4$ mixture was probably due to a decrease in L_d.

3.7 Effect of particle size on linear burning rate

According to the GDF model [8], which was found to be adequate for describing the burning behavior of ammonium perchlorate (AP) - based composite propellants, *r* is affected by the diameter of the oxidizer particle; reducing the diameter of the oxidizer increases *r*. On a burning surface of AP-based composite propellant, polymer resin that surrounds AP particles decomposes at the burning surface, releasing pockets of fuel gases with diameters equal to diameters of oxidizer particles from the burning surface, and then undergoes combustion in the midst of pockets of gas products of oxidizer decomposition.

Effect of particle size on pressure-time curve is given in Fig. 5. Reducing the sizes of fuel particles and reducing the size of oxidizer particles have led to an increase in the pressure gradient for each case. This was probably due to an increase in *r* for each case, taking into consideration that the composition of the samples and the mixing ratios are kept constant. In addition, it was clarified that the phenomenon in which *r* have increased with a decrease in particle size could be explained by the GDF model.

4. Conclusions

Evaluations of combustion characteristics of gas generating agents for automobile airbag inflators have been conducted for 5-ATZ / $LiClO_4$ / CuO mixtures by using closed chimney-type strand burner. As a result, the following conclusions were obtained for *r*, the pressure-time history, the temperature-time history and burning mechanism.

1) Addition of small amount (4.3 wt%) of CuO into 5-ATZ / $LiClO_4$ mixture has led to an increase in *r* and the pressure gradient, and to a decrease in the temperature of generated gases. However, *r* was found to decrease with the addition of relatively large quantities (19.4 wt%) of CuO.
2) The main reason for an increase in *r* with the addition of small amount of CuO was probably due to the shortening of diffusion distance, which has led to the flame approaching the burning surface, hence to an increase in the amount of heat transfer.
3) The main reason for a decrease in *r* with the addition of excessive CuO was probably due to an increasing amount of 5-ATZ / CuO mixture, which has a relatively low adiabatic flame temperature, hence leading to a decrease in heat transfer from the flame to the burning surface of 5-ATZ / $LiClO_4$ / CuO mixtures.
4) Burning behaviors of the samples used in this experiment were found to be well explained by the GDF model which was proposed by Summerfield et al.

References

1) J. Z. Wu, M. Wakakura, T. Matsuzawa, M. Arai, and M. Tamura, Kayaku Gakkaishi (Sci. Tech. Energetic Materials), 55, 74 (1994).
2) J. Z. Wu, J. M. Chen, M. Itoh, M. Arai, M. Tamura, T. Andoh, and S. Morisaki, *ibid.*, 55,188 (1994).
3) J. Z. Wu, H. Yuzawa, T. Matsuzawa, M. Arai, and M. Tamura, *ibid.*, 55, 66 (1994).
4) K. Hasue, T. Akanuma, H. Hodai, and S. Date, *ibid.*, 60, 31 (1999).
5) K. Hasue, P. Boonyarat, Y. Miyata, and J. Takagi, *ibid.*, 62,168(2001).
6) Y. Miyata, S. Date, and K. Hasue, Propellants, Explosives, Pyrotechnics, 29, 247 (2004).
7) Y. Miyata, H.Kanou, S. Date, and K. Hasue, Sci. Tech. Energetic Materials, 233, 66 (2005).
8) M. Summerfield, G. S. Sutherland, M. J. Webb, H. J. Taback, and K. P. Hall, Solid Propellant Rocket Research, Vol. 1, Academic Press, New York and London (1960) 141.
9) K. Hara, T. Yoshida, T. Misawa, T. Maekawa, S. Yoshi, T. Yokoyama, T. Kazumi, and M. Hayashi, Propellants, Explosives, Pyrotechnics, 23, 28 (1998).
10) S. Date, P. Boonyarat, T. Kazumi, and K. Hasue, Kayaku Gakkaishi (Sci.Tech.Energetic Materials), 63, 209 (2002).
11) Y. Miyata, S. Date, and K. Hasue, Sci.Tech.Energetic Materials, 65,167 (2004).
12) F. Volk and H. Bathelt, User's manual for the ICT-Thermodynamic Code (1998), Fraunhofer-Institut für Chemische Technologie, Pfinztal.

5-amino-1H-tetrazole と過塩素酸リチウム混合物の燃焼に対する酸化銅(II)の影響(第1報)
−燃焼機構について−

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5-amino-1H-tetrazole (5-ATZ) は，自動車用エアバッグに使用されているアジ化ナトリウムに代わる燃料成分として注目されている。酸化剤として用いた過塩素酸リチウムは，酸素含量が多い。本研究では，5-ATZと過塩素酸リチウム混合物の燃焼及び酸化銅 (II) 添加の影響について調べた。5-ATZと過塩素酸リチウム混合物の線燃焼速度は，実用化されている5-ATZ／硝酸ストロンチウム混合物より速く，単位質量当たりのガス発生量が多いことがわかった。また，拡散粒状火炎モデルが適用できるかどうか検討し，1-5MPaの試験範囲で，拡散過程が線燃焼速度に影響することを見いだした。酸化銅(II)を少量添加すると線燃焼速度が増加するのは，拡散距離を短くなり，火炎が燃焼表面に接近し，フィードバック熱量が増すためと思われる。

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