

Effect of the particle size of ferric oxide on the thermal decomposition of AP-HTPB composite propellant

Kaori Fujimura[†] and Atsumi Miyake

Yokohama National University, 79-7 Tokiwadai, Hodogaya, Yokohama, Kanagawa 240-8501, JAPAN

[†]Corresponding address: d07tf008@ynu.ac.jp

Received: April 7, 2008 Accepted: July 14, 2008

Abstract

Thermal analysis was carried out to investigate the effect of the particle size of ferric oxide, which acts as a combustion catalyst, on the thermal decomposition of a solid propellant consisting of ammonium perchlorate (AP) as an oxidizer and hydroxyl-terminated polybutadiene (HTPB) as a binder. The particle size of ferric oxide used in this study varied from nanometer size to submicron size. Differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were used for the investigation of the thermal behavior of the samples. The activation energy was calculated using the Kissinger method. As a result, it was confirmed that the size reduction of Fe_2O_3 to nanometer size contributes to the promotion of the decomposition of AP-based solid propellant with the lowering of reaction temperature and / or activation energy.

Keywords: Solid propellant, Nano ferric oxide, Ammonium perchlorate, Catalysis, Thermal analysis.

1. Introduction

Burning rate and specific impulse are representative parameters that describe the burning characteristics of solid propellants. In order to design rocket motors, the basic method to satisfy the required relationship between impulse and combustion time of the rocket motor is the adjustment of the burning area by tailoring the grain configuration of the propellant. However, controlling the burning rate more widely would be very advantageous in designing rocket motors because the restriction on grain configuration could be decreased. Representative methods to control the burning rate of composite solid propellants used to date include: 1) adding a combustion catalyst,^{1)~9)} 2) controlling the particle size of the solid oxidizer,^{10), 11)} 3) increasing thermal conductivity¹²⁾ and 4) increasing of the heat transfer coefficient.

It is well known that the burning rate of the composite propellant which consists of ammonium perchlorate (AP) is enhanced when some transition metal oxides (TMOs) are added to the compositions.^{1), 2), 6), 7)} For example, ferric oxide (Fe_2O_3), copper oxide (CuO or Cu_2O), copper chromate (CuCrO_4), copper chromite (CuCr_2O_4) and manganese oxide (MnO_2) are very effective in enhancing burning rate. Among these TMOs, Fe_2O_3 has been used most commonly, therefore its catalytic effect has been researched widely.^{1), 2), 7)} Although many researchers have proposed

various ideas about how Fe_2O_3 enhances the burning rate, it still remains unclear. In such research it also has been pointed out that the particle size of the combustion catalysts greatly effects the burning rate enhancement. However there have been few studies in which the particle size effect was confirmed experimentally. Recently, nano-sized particles have become available at a relatively low price, but there have been few reports of these nanosized particles applied to composite propellants as combustion catalysts.^{7)~9)}

In a previous report, the effect of the particle size of Fe_2O_3 on the burning rate of AP / HTPB composite propellants was examined with a series of combustion tests.¹³⁾ It was clear that the burning rate was greatly enhanced by reducing the size of Fe_2O_3 from submicron to nanometer size. In the present study, the effect of Fe_2O_3 particle size on the decomposition of AP / HTPB composite propellant was examined by thermal analysis. To examine the effect on AP decomposition, which is considered to be the first step of propellant decomposition, thermal analysis was also carried out for the AP / Fe_2O_3 mixture. For convenience, the size reduction to nanometer size is defined as “nanosization” in this paper.

Table 1 Compositions of the solid propellant samples (by parts).

Sample No.	Solid oxidizer	Binder	Combustion catalyst	
	AP	HTPB	Fe ₂ O ₃ (f)	Fe ₂ O ₃ (c)
1	84	16	1.0	—
2	84	16	—	1.0
3	84	16	—	—

Table 2 Compositions of the AP / Fe₂O₃ mixture samples (by parts).

Sample No.	Solid oxidizer	Combustion catalyst	
	AP	Fe ₂ O ₃ (f)	Fe ₂ O ₃ (c)
4	100	1.2	—
5	100	—	1.2
6	100	—	—

2. Experimental

2.1 Materials

Two series of samples were prepared in this study: solid propellant samples and AP / Fe₂O₃ mixture samples. Table 1 shows the main compositions of the solid propellant samples. In addition to the listed materials, the solid propellant samples included a small amount of plasticizer and curing agent. Two types of Fe₂O₃ were used: a fine one which had mean particle sizes of 5.4 nm, called Fe₂O₃(f), and a coarse one with particle sizes of 0.36 μ m, called Fe₂O₃(c). These sizes were confirmed with small-angle X-ray scattering (SAXS) or dynamic light scattering (DLS), respectively.¹³⁾ The compositions were confirmed by powder X-ray diffraction using a Shimadzu XRD-6000, so any materials other than Fe₂O₃ were not detected.

Table 2 shows the compositions of the AP / Fe₂O₃ mixture samples. Sample No. 6 was pure AP with no Fe₂O₃. The particle size of AP used in these samples was 10 μ m. The two kinds of Fe₂O₃ used were the same as mentioned above. To prepare the AP / Fe₂O₃ mixture samples, both AP and Fe₂O₃ were heated separately at 373 K for two hours in a furnace to eliminate moisture. The designated weights of AP and Fe₂O₃ were then measured and simply mixed with a wooden stick in a mortar. The ratio of AP and Fe₂O₃ in these mixture samples was equivalent to the ratio of those in the propellant samples.

2.2 Thermal Analyses

DSC measurements were carried out on a Mettler-Toledo differential scanning calorimeter, DSC822e. The sample was placed in an aluminum pan and then the pan was crimped to withstand an internal pressure of about 0.2 MPa. The weights of the solid propellant samples and AP / Fe₂O₃ mixture samples were about 1.5 mg and 0.5 mg, respectively. The dynamic scans were performed at a heating rate of 1, 3, 5, 10 and 20 Kmin⁻¹, in a temperature range from 293 K to 773 K. During the measurement, nitrogen gas was purged throughout the system at 50 mLmin⁻¹ to maintain an inert environment.

TGA and DTA measurements were carried out on a TGA / SDTA851e (Mettler-Toledo) which could measure TGA and DTA curves simultaneously. The sample (about 3.0 mg) was placed in an alumina pan which was covered with a pierced lid. The dynamic scans were performed at a heating rate of 3, 5, 8 and 10 Kmin⁻¹, in a temperature range from 303 K to 873 K. During the measurement, nitrogen gas was purged throughout the system at 50 mLmin⁻¹ to maintain an inert environment.

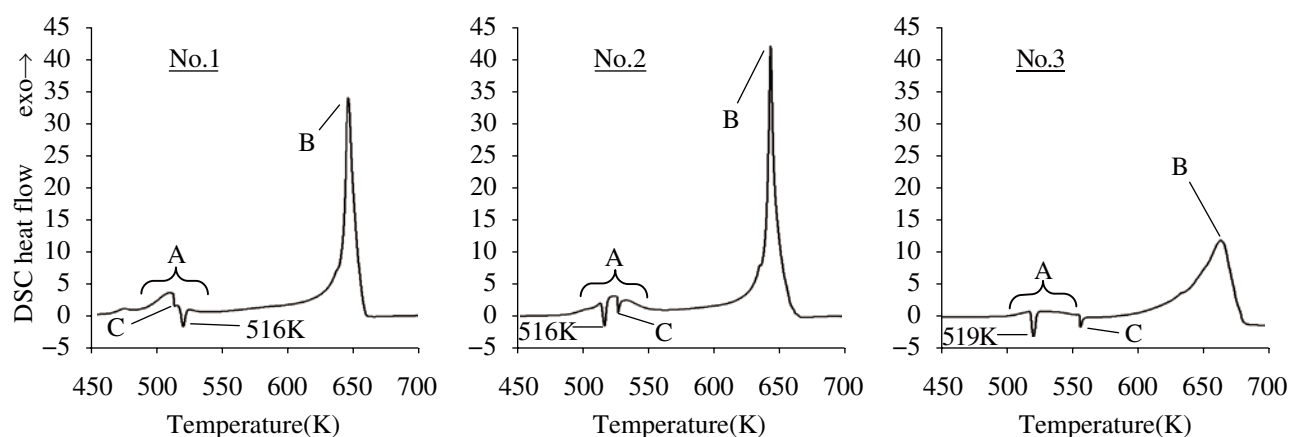
For both instruments, the Star_e software (Mettler-Toledo) was used to control the temperature program and obtain thermograms for analysis.

3. Results and Discussion

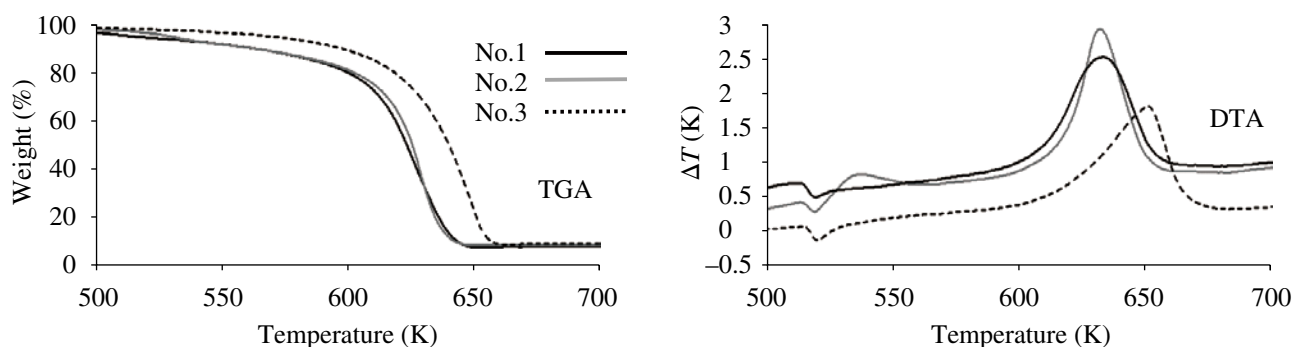
3.1 Propellant Samples

The DSC curves of the solid propellant samples at a heating rate of 10 Kmin⁻¹ are shown in Fig. 1. In each curve four thermal events are observed: a broad exothermic peak (A) at 490 - 530 K, a large exothermic peak (B) over 620 K, a shifting small endothermic peak (C) between 500 K to 550 K and a small endothermic peak near 520 K. The peak temperatures T_p of peaks A, B and C in Fig. 1 are summarized in Table 3. The peak temperature was measured at least three times per a sample and then averaged. The TGA and DTA curves at a heating rate of 10 Kmin⁻¹ are shown in Fig. 2.

The endothermic peak near 520 K in the DSC and DTA curves for each sample can be attributed to the phase transition of AP from the orthorhombic to cubic form.^{14), 15)} This is supported by the fact that the TGA curve does not show a weight loss at this temperature. There is another endothermic peak (peak C) in the DSC curve at 555 K for sample No. 3 and 525 K for sample No. 2. For sample No. 1, the peak shifts to even lower temperature, 510 K. Since there is no weight loss observed in the TGA curves at this temperature, it is believed that this peak represents the scission of polymer binder. The order of this temperature shift is No. 1 > No. 2 > No. 3. Since the burning rate order obtained from the combustion test is also No. 1 > No. 2 > No. 3,¹³⁾

Fig. 1 DSC curves of solid propellant samples (heating rate: 10 Kmin⁻¹).Table 3 Peak temperature T_p of solid propellant samples (K).

Sample No.	Peak A (exothermic)	Peak B (exothermic)	Peak C (endothermic)
1	506	648	510
2	522	648	526
3	526	667	555

Fig. 2 TGA and DTA curves of solid propellant samples (heating rate: 10 Kmin⁻¹).

it is concluded that this drop in the endothermic reaction temperature in the DSC curve may be related to the burning rate enhancement and that the nanosization of the Fe_2O_3 particles further promotes the effect. No endothermic peaks were detected in the DTA curves at this temperature. This may be attributed to the lower resolution of DTA.

The small exothermic peak (peak A) at 490 - 530 K for each sample is difficult to distinguish, because the shape of this peak is very broad and it overlaps the endothermic peak. It is believed that this peak represents the decomposition of the binder because a gentle weight loss curve can be seen in the TGA curves of samples No. 1 and 2. The temperature shift of this peak increases in the order of No. 1 > No. 2 > No. 3 as the particle size of Fe_2O_3 gets smaller. Therefore it is concluded that this drop in the reaction temperature may relate to the improvement of the burning rate and that the nanosization of the Fe_2O_3 particle further promotes the effect in a similar manner to peak C. Fong et al. proposed that Fe_2O_3 catalyzes the melting or thermal decomposition of the binder.³⁾ These results support their proposal.

The largest peak at higher temperature, peak B corresponds to the exothermic decomposition of AP. This peak shifts to low temperature by the addition of Fe_2O_3 in a similar manner as the other peaks. This peak is characterized by a change of the peak configuration especially in samples No. 1 and No. 2 and suggests that the reaction became more dramatic by the addition of Fe_2O_3 . It has been stated that Fe_2O_3 has a catalytic effect on the decomposition of AP and the mechanism of the catalytic effect has been proposed in many times.^{16) ~ 19)} This change of the peak configuration supports those opinions. However the nanosization of the Fe_2O_3 particles seems to have no effect on this peak.

In the present study, it is assumed that each reaction follows the Arrhenius equation,

$$k = A \exp(-E_a / RT) \quad (1)$$

where k is the rate constant, E_a is the activation energy, R is the gas constant, T is the absolute temperature and A is the frequency factor. In this case, the thermal stability of

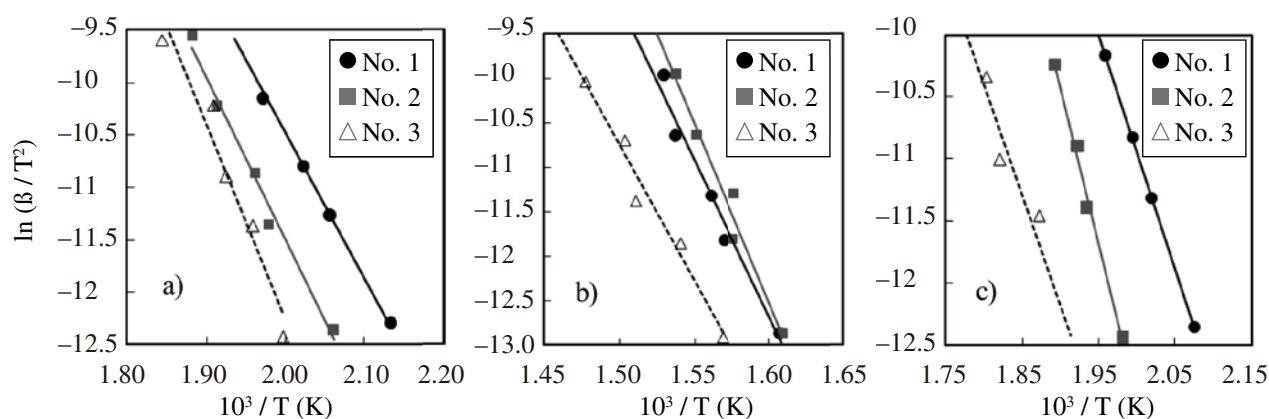


Fig. 3 Kissinger plots for solid propellant samples, a) peak A, b) peak B, c) peak C.

Table 4 Activation energy of solid propellant samples (kJmol⁻¹).

Sample No.	Peak A (exothermic)	Peak B (exothermic)	Peak C (endothermic)
1	116	278	146
2	129	311	196
3	144	233	133

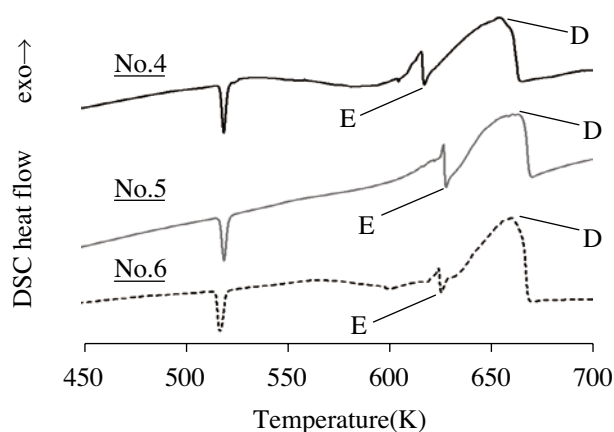


Fig. 4 DSC curves of AP / Fe₂O₃ mixture samples (heating rate: 10 Kmin⁻¹).

the samples at various heating rates can be analyzed using a Kissinger plot in which $\ln(\beta / T_p^2)$ versus $1 / T$ plot shows a linear relationship as shown in the following equation,

$$\ln(\beta / T_p^2) = -E_a / RT_p + \ln(AE_a / R) \quad (2)$$

where β is the heating rate and T_p is the peak temperature.²⁰⁾ This equation can be rearranged to the following form,

$$E_a = R \frac{d \ln(\beta / T_p^2)}{d(1 / T_p)} \quad (3)$$

Kissinger plots for each peak are shown in Fig. 3 and the activation energy calculated by those plots is summarized in Table 4.

Compared to the result of the peak temperature, it was revealed that the order of the activation energy was not necessarily the same as that of the temperature shift. Especially for peak B, which represents the main reac-

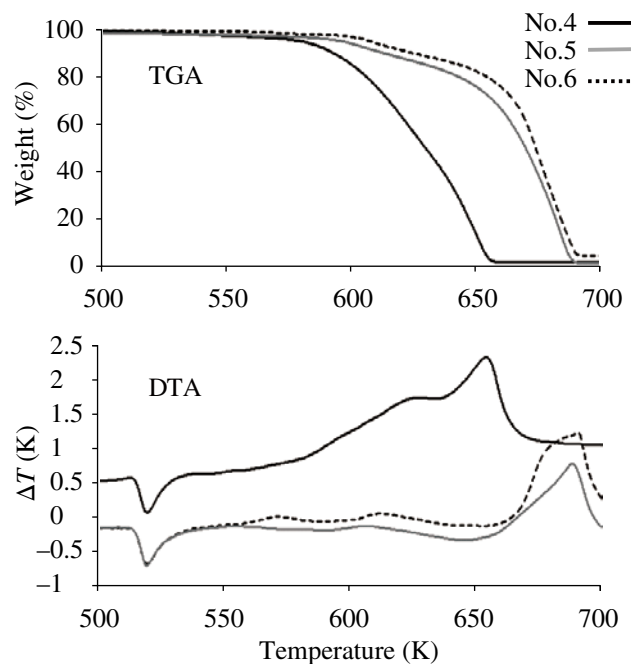


Fig. 5 TGA and DTA curves of AP / Fe₂O₃ mixture samples (heating rate: 10 Kmin⁻¹).

tion, the activation energy increases remarkably with the addition of Fe₂O₃. It was concluded that the use of Fe₂O₃ and nanosization contributed to peak A by lowering both the reaction temperature and activation energy, while they contributed to peak B and C only by lowering the reaction temperature. Since the reaction order cannot be determined from the measurements in this study, frequency factor A, which provides a measure of the frequency of occurrence of the reaction situation, cannot be calculated. Its determination is the object of a future study.

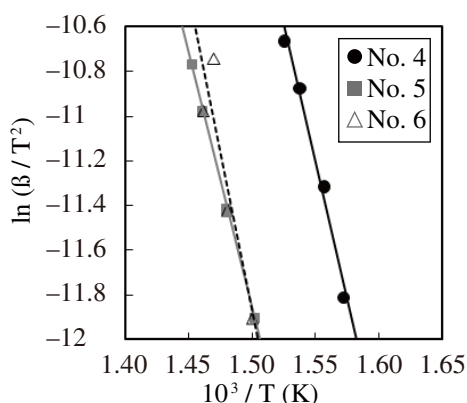


Fig. 6 Kissinger plots for AP / Fe₂O₃ mixture samples.

3.2 AP / Fe₂O₃ Mixture Samples

The DSC curves of the AP / Fe₂O₃ mixture samples at a heating rate of 10 Kmin⁻¹ are shown in Fig. 4. In each curve, three thermal events are observed: a large exothermic peak (D) at around 670 K, an endothermic peak (E) at around 630 K and an endothermic peak near 520 K. All curves are of the same shape with no significant differences.

The TGA and DTA curves at a heating rate of 10 Kmin⁻¹ are shown in Fig. 5. In this figure there is a remarkable difference in the curve shapes. In the TGA curves, sample No. 4 starts a weight loss at a lower temperature than No. 5 and No. 6 and the DTA curve shows an exothermic peak at the same temperature of the weight loss in the corresponding TGA curve. The shape of this exothermic peak in the DTA curves seemed to be one peak for No. 5 or No. 6, but two peaks are clearly observed for No. 4. The reason why this peak is not observed in the DSC curves but appeared in the DTA curves is believed to be due to the difference in the sealing state of the samples. This technical issue requires further consideration.

A Kissinger plot for the main exothermic peak in the DTA curves is shown in Fig. 6 and the kinetic data calculated with the plot are summarized in Table 5. The order of the activation energy for this peak is No. 4 < No. 6 < No. 5. Fig. 6 shows that the line of No. 4 shifts more towards the right than those of No. 5 and No. 6. Thus it is clear that the addition of micro-sized Fe₂O₃ does not affect the activation energy very much, while the addition of nano-sized Fe₂O₃ decreases it greatly. It can therefore be concluded that the nanosization of Fe₂O₃ contributes to AP decomposition both by lowering the reaction temperature and the activation energy.

Conclusions

From the results of thermal analysis, it was confirmed that the use of Fe₂O₃ and its nanosization, in particular, contribute to the decomposition of composite solid propellant including AP by both lowering the reaction temperature and/or the activation energy. And it was also clear that nanosization of Fe₂O₃ contributes to AP decomposition by both of lowering the reaction temperature and the activation energy. It can be assumed that these nanosization effects enhance the burning rate of the solid propellant further.

Table 5 Activation energy of peak D of AP / Fe₂O₃ mixture samples (kJmol⁻¹).

Sample No.	Peak D (exothermic)
4	131
5	170
6	156

Acknowledgements

This research was supported by the Technical Research & Development Institute in the Ministry of Defense. And we would like to acknowledge Asahi Kasei Chemicals Corporation for their assistance with the preparation of samples.

References

- 1) S. Krishnan and R. Jeenu, J. Propulsion and Power, 8, 748 (1992).
- 2) S. R. Chakravarthy, E. W. Price and R. K. Sigmant, J. Propulsion and Power, 13, 471 (1997).
- 3) C. W. Fong and B. L. Hamshire, Combustion and Flame, 65, 61 (1986).
- 4) C. W. Fong and B. L. Hamshire, Combustion and Flame, 65, 71 (1986).
- 5) B. L. Dubey, N. Nath, A. Tripathi and N. Tiwari, Indian Journal of Engineering and Materials Sciences, 1, 341 (1994).
- 6) G. S. Pearson, Combustion and Flame, 14, 73 (1970).
- 7) P. R. Patil, V. N. Krishnamurthy and S. S. Joshi, Prop., Explos., Pyrotech., 6, 442 (2006).
- 8) W. Li and H. Cheng, Solid State Science, 9, 750 (2007).
- 9) J. L. Small, M. A. Stephens, S. Deshpande, E. L. Peterson and S. Seal, Proceedings of the 20th International Colloquium on the Dynamics of Explosions and Reactive Systems, Montreal, July 31 - August 5 (2005).
- 10) A. Pivkina, Yu. Frolov and D. Ivanov, Combust., Expl., Shock Waves, 43, 51 (2007).
- 11) K. M. Ide, DSTO Report, DSTO - GD - 0344 (2002).
- 12) L. H. Caveny and R. L. Glick, J. Spacecraft and Rockets, 4, 79 (1967).
- 13) K. Fujimura, Technical Report No. 6915, Technical Research and Development Institute, Japan Defense Agency (2006).
- 14) S. H. Shen, S. I. Chen and B. H. Wu, Thermochim. Acta, 223, 135 (1993).
- 15) J. A. F. F. Rocco, J. E. S. Lima, A. G. Frutuoso, K. Iha, M. Ionashiro, J. R. Matos and M. E. V. Suarez-Iha, J. Therm. Anal. Cal., 75, 551 (2004).
- 16) Z. Ma, F. Li and H. Bai, Prop., Explos., Pyrotech., 31, 447 (2006).
- 17) E. Santacesaria and A. Morini, Combustion and Flame, 31, 17 (1978).
- 18) F. Solymosi, L. Gera and S. Börcsök, Proceeding of Combustion Institute vol. 13, pp. 1009 - 1018 (1970).
- 19) T. L. Boggs, D. E. Zurn, H. F. Cordes and J. Corino, Journal of Propulsion, 4, 27 (1988).
- 20) H. E. Kissinger, Anal. Chem., 29, 1702 (1957).

AP-HTPB系コンポジット推進薬の熱分解に及ぼす 酸化鉄粒径の効果

藤村郁子[†], 三宅淳巳

酸化剤として過塩素酸アンモニウム (AP), バインダーとして末端水酸基ポリブタジエン (HTPB) から成る固体推進薬の熱分解に与える, 燃焼触媒として作用する酸化鉄の粒径効果を調べるために, 熱分析を実施した。本研究で使用した酸化鉄の粒径は, ナノメートルサイズからサブミクロンサイズである。サンプルの熱挙動の観察には示差走査熱量測定 (DSC), 熱重量測定 (TGA) 及び示差熱分析 (DTA) を使用した。活性化エネルギーは Kissinger 法を用いて計算した。結果として, Fe_2O_3 のナノ化は AP を含むコンポジット固体推進薬の分解反応の促進に対して反応温度 and / or 活性化エネルギーの低下という形で寄与することがわかった。

横浜国立大学大学院 〒240-8501 神奈川県横浜市保土ヶ谷区常盤台79-7

[†]Corresponding address: d07tf008@ynu.ac.jp