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Influence of iron oxide on thermal decomposition behavior and burning characteristics of ammonium nitrate/ammonium perchlorate-based composite propellants

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ABSTRACT

The thermal decomposition behavior and burning characteristics of ammonium nitrate(AN)/ammonium perchlorate(AP) propellants supplemented with Fe_2O_3 were investigated. Based on these data, the performance differences between the propellants with Fe_2O_3 and those without Fe_2O_3 were investigated to reveal the influence of Fe_2O_3 on the thermal decomposition behavior and burning characteristics of AN/AP-based composite propellants. TG-DTA showed the peak temperature and temperature range of thermal decomposition due to AN decomposition to be independent of the presence of Fe_2O_3. The peak and the offset temperature of thermal decomposition due to AP decomposition decreased owing to the addition of Fe_2O_3, while the onset temperature did not vary. The burning rate of the AN/AP propellant was increased by the addition of Fe_2O_3; the effect of Fe_2O_3 on increasing the burning rate was influenced by the type of oxidizer, AP content in the oxidizer (ξ), and AP size. Furthermore, Fe_2O_3 allowed the suppression of the remarkable heterogeneity of the combustion wave of the AN/AP propellant without Fe_2O_3. The ignitability of the AN/AP propellant was improved by the addition of Fe_2O_3, except for the propellant with a ξ of 0.4. The cause of depressed ignitability by the addition of Fe_2O_3 for the propellant with a ξ of 0.4 is discussed based on thermogravimetry-differential thermal analysis, the visual observations of the unignited propellant surfaces, and the decomposition phenomena of the propellants using a high-temperature observation equipment. A large quantity of AN remained on the surface of the unignited propellant at 0.5 MPa. The cause of the depressed ignitability is that AN, AP, and HTPB do not simultaneously decompose and as a result AN remains on the burning surface. Thus, the burning surface of AN did not regress simultaneously with the burning surface of the AP-filled region, the matrix of AP, and HTPB.

1. Introduction

Solid propellants are commonly used as propulsion fuels for space launch vehicles, spacecraft, missiles, and other applications. There are various types of solid propellants, and a suitable propellant is selected to meet the requirements of each particular rocket motor application. Therefore, the development of a wide variety of rockets requires the development of propellants with wide ranging performance, in accordance to their intended purpose. A composite propellant is a type of solid propellant consisting of an oxidizer, binder curing agent, metal fuel, burning catalyst, and other components. Several composite propellants were prepared with various types of propellant ingredients and their burning characteristics were investigated.

Ammonium perchlorate (AP) is the most widely used oxidizer in composite propellants, because AP-based propellants have excellent burning characteristics. To date, many researchers have studied the burning characteristics and combustion wave structure of AP-based composite propellants [1–5]. The burning rate can be controlled by the physical properties of the combustion wave structure; it is known that the burning rate of propellants greatly increases with decreasing mean diameter of AP particles [2,6–9].

Recently, ammonium nitrate (AN)-based composite propellants, i.e., propellants prepared with AN as the oxidizer, have gained popularity because of their low cost and easy availability, even though there are some major problems associated with the use of AN-based propellants, namely, low burning rate, poor ignitability, and low energy compared to AP-based propellants [10]. The addition of a burning catalyst is a useful way to improve these disadvantages of propellant performance [10–21]. The burning characteristics of the AN propellant were also improved by the addition of nitramines, such as hexogen and octogen, because of the high

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Nomenclature

Chemicals

AN	ammonium nitrate
AP	ammonium perchlorate
HTPB	hydroxyl-terminated polybutadiene

Acronyms

CAP	coarse AP
DMS	digital microscope
DTA	differential thermal analysis
DTG	differential thermogravimetry
FAP	fine AP
PDL	pressure deflagration limit
SEM	scanning electric microscopy
TG	thermogravimetry

Symbol

R	ratio of the burning rate of propellant with Fe_2O_3 to that of the corresponding propellant without Fe_2O_3
T_1	peak temperature of first decomposition
T_2	peak temperature of second decomposition
ξ	AP content in oxidizer

energy of nitramine [22,23]. Furthermore, the burning rate of the AN/hexogen propellant was increased by using either MnO_2 or Fe_2O_3 as a catalyst [24]. As described above, AP-based propellants have excellent burning characteristics. The addition of AP to AN-based propellants allows the significant increase of the propellant's burning rate, ignitability, and energy density. For AN/AP-based propellants, the drawbacks of AN are improved by the advantages of AP. Some success has been achieved in overcoming the problems of burning characteristics by the substitution of AP with AN [25–29].

As described above, the burning rate of the AP propellant depends on the size of AP, while that of the AN propellant does not depend on the size of AN [30]. Kohga *et al.* [27] reported the burning characteristics of AN/AP-based composite propellants prepared with AP of various particle sizes and its combustion wave structure model. The burning behavior of AN/AP propellants was dependent on the particle size of AP and AP content in the oxidizer (ξ). The burning rate increased with increasing ξ, and the burning rate increment increased as the particle diameter of AP decreased. Some propellants, prepared with a small AP below 69 µm (SAP) at a ξ of 0.4 and 0.6, displayed a self-quenched or unstable burning behavior; partial flashing flame, and flame propagation along the side of the propellant.

Figure 1 shows the combustion wave models of AN/SAP/HTPB-based propellants [27]. For the model of AN/HTPB propellant ($\xi = 0$), Fig. 1(a), the condensed phase is formed just under the burning surface by the melting of AN, which melts endothermically. Subsequently, AN evaporates/decomposes around the burning surface by the absorption of the heat flux feedback from the flame [31]. HTPB would rarely decompose in the condensed phase but it would decompose at the burning surface. The decomposition gases of AN and HTPB diffuse into the gas phase and burn. The combustion of AN propellant depends on the dominant reaction in the condensed phase, especially the dissociative evaporation of AN [26,32].

The flame of the AP-based propellant is called diffusion flame, and the multiple-flame model [33] is generally accepted as the flame structure model. Figure 1(c) shows the model of the SAP/HTPB propellant ($\xi = 1$). The burning surface is heated with both the heat flux feedback from the flame and the heat generated by the exothermic decomposition of SAP. SAP and HTPB decompose at the burning surface. The decomposition gases diffuse into the gas phase and combust.

The model of the AN/SAP/HTPB propellant ($\xi = 0.2$–0.8) is shown at Fig. 1(b). AN melts and subsequently evaporates/decomposes. The condensed phase is formed just under the burning surface and its thickness decreases with increasing ξ. SAP and HTPB decompose at the burning surface and rarely melt before decomposition. The combustion reaction rate of AP and HTPB is higher than that of AN and HTPB [31]. Since SAP is a small particle, it is supposed to disperse in HTPB, and AN scatters in the matrix of SAP and HTPB which is described as an AP-filled region. In this case, it is assumed that AN/SAP/HTPB propellant consists of an AN and AP-filled region to simplify the combustion model. Since SAP and HTPB simultaneously decompose at the burning surface, the AP-filled region had an almost flat burning surface. To sustain the steady combustion of AN and AP-filled region, these decomposition gases should be evolved continuously by the heat flux from the gas phase and the heat generated at the burning surface. Eventually, the decomposition gases of AN and the AP-filled region are burned. It is required that the burning surface of AN would regress almost simultaneously with that of the AP-filled region, that is, the regression rate of AN should be almost the same as that of the AP-filled region. The reason for the unstable combustion of some AN/SAP/HTPB propellants ($\xi = 0.4$ and $\xi = 0.6$) was the difference in the regression rate between AN and AP-filled region, i.e., the remarkable heterogeneity of the combustion wave structure of the propellant [27].

To apply the AN/AP based composite propellant to practical use, it is necessary to inhibit the remarkable heterogeneous combustion wave structure of the propellant with the self-quenched or unstable combustion. As described above, the development of propellants with wide performance range is required to meet the demands of various rocket applications. Fe_2O_3 is an effective burning catalyst for both AP- and AN-based propellants. It was expected that the addition of Fe_2O_3 to the AN/AP propellants would not only inhibit the self-quenched and unstable combustion, but also increase the burning rate.

In this study, the thermal decomposition behavior and burning characteristics of AN/AP propellants supplemented with Fe_2O_3 were investigated. Coarse AP (CAP) and fine AP (FAP) were used in this investigation because the behavior of the AN/AP propellant without Fe_2O_3 was influenced by the size of AP; in particular, the AN/FAP propellant exhibited a self-quenched or unstable burning behavior [27]. Based on these data, the performance differences between the propellants with Fe_2O_3 and those without Fe_2O_3 were investigated to reveal the influence of Fe_2O_3 on thermal decomposition behavior and the burning characteristics of AN/AP-based composite propellants. The details of these results are presented in this paper.

2. Experiment

2.1. Materials and propellant samples

AN and AP were used as oxidizers. An AN sample was prepared by grinding a commercial AN with a vibration ball mill for 5 min. CAP was prepared by grinding a commercial AP with a vibration ball mill for 5 min. FAP was prepared by the freeze-drying method [34]. The mean particle diameters of AN, CAP, and FAP were 56, 180, and 3 µm, respectively. The burning characteristics of the AN/AP propellant hardly depend on the AN particle size because the dependence of the AN size on the burning characteristics is little [30]. Therefore, one size of AN sample was used in this study. HTPB was used as a binder. The propellant sample contained 80% oxidizer and 20% HTPB. Fe_2O_3 was used as a burning catalyst because it is a useful catalyst for both AP and AN propellants.