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Note

Role of condensed-phase reactions during the ignition of a composite solid propellant

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Ignition studies of composite solid propellants are important to understand their initial ignition behavior in the rocket motor. A lot of work has been carried out to understand the ignition process in the past[1-5]. Most of the work, however, deals with the analytical theories for the ignition of solid propellants. Although these theories take into account some of the experimental facts, the validity of any theory in totality is still a matter of controversy. It is generally accepted that the ignition is preceded by a growth of exothermic chemical reactions in the propellant bulk. The objective of the present work, therefore, is to examine the role of condensed-phase reaction during ignition.

In a recent work by the same authors[6], it has been shown that the ignition temperature (determined by DTA technique) of polystyrene (PS)/ammonium perchlorate (AP) propellant with and without Fe_2O_3 additive is correlated with the thermal decomposition of the propellant itself and the thermal decomposition of AP contained in it. This particular study was made in air at atmospheric pressure. In the present investigation the ignition experiments were carried out in vacuum. The ignition experiments in vacuum (5×10^{-2} mm Hg) were carried out by placing the sample (~300 mg) at the bottom of a long pyrex tube connected to a rotary vacuum pump and tilting McLeod gauge. The propellant sample was heated isothermally by introducing the furnace maintained at a particular temperature (350 °C) around the tube containing the sample.

In order to test the temperature at which the propellant ignition starts (with the appearance of visible flame) separate experiments were carried out by dropping the propellant of a definite weight (~300 mg) and shape (rectangular block) in a tubular furnace maintained at a particular temperature. It was observed that the propellant does not ignite below 270 °C. The condensed-phase heat release during the thermal decomposition of PS/AP (75%) has

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been calculated from the DSC thermogram[7]. A typical DSC thermogram under scanning conditions is shown in Fig. 1.

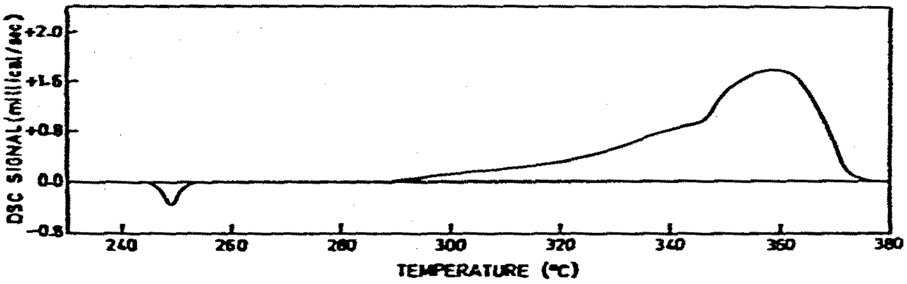

Fig. 1. Typical differential scanning thermogram of PS/AP propellant. Scan rate, 8 °C min^{-1}; sample weight, 0.695 mg.

Figure 1 shows that exothermic reactions in the propellant start taking place only above 280 °C. The fact that the propellant does not ignite below 270 °C and that the exothermic reactions in the propellant, on heating, start taking place only after 280 °C suggests that the generation of condensed-phase heat is extremely essential for the propellant ignition. This observation supports the thermal ignition theory[4], according to which ignition is primarily controlled by condensed-phase heat release.

In the thermal ignition theory[4] the ignition delay (τ) and the ignition temperature (T_i) are related according to the following equation

$$\tau^{1/2} = \frac{K}{2\dot{Q}}(T_i - T_o)\left(\frac{\pi}{\alpha}\right)^{1/2} \tag{1}$$

where

T_o = initial temperature (°C) of the propellant
K = thermal conductivity (cal cm^{-1} sec^{-1} deg^{-1}) of the propellant
$\dot{Q}$ = heating rate (deg sec^{-1})
a = thermal diffusivity (cm^2 sec^{-1})

For a composite propellant an approximate estimate of T could be made from the above equation by using the following physico-chemical data for the AP/PS propellant: $k = 0.0006$; $a = 0.001$; $\dot{Q} = 0.111$; $T_o = 23$ °C; $T_i = 322$ °C.

Calculated ignition delay (T) from eqn (1) appears to be 35 minutes, whereas the experimental value is 43 min[6], which is in good agreement with the thermal ignition theory. This shows the importance of condensed-phase heat release for the ignition of the propellant. Kirby and Suh[8] have described a method by which the condensed-phase heat release could be estimated. The equation used for such a calculation is given below.

$$\Delta H = C_p(T_s - T_o) \tag{2}$$

Where ΔH is the condensed-phase heat release in cal g^{-1}. T_s is the minimum surface temperature with no heat feed back from the gas phase and T_0(°C) is the ambient temperature. T_s can be safely taken to be the ignition temperature (T_i) of the propellant. For the PS/AP propellant, the calculated value of ΔH from eqn (2) is 100 cal g^{-1} (C_p is taken to be 0.35 cal g^{-1} deg^{-1}). From the DSC thermogram (heating rate of propellant, 8 °C min^{-1}), presented in Fig. 1, ΔH at the ignition temperature for the PS/AP propellant could be estimated and was found[7] to be 75 cal g^{-1}. Judging from the fact that the above calculated ΔH values at the ignition temperature are from two independent experiments and approaches, the agreement is not bad. This once again shows that condensed-phase heat release is related to the ignition temperature of the propellant.

From the facts presented above, the exothermic condensed-phase reaction appears to play a significant role during the propellant ignition process. However, one may argue that other theories[1-4] also control the ignition process, unless proved otherwise. It may be noted here that the hypergolic ignition theory need not be considered since no reactive oxidisers have been used for ignition to occur.

In our ignition delay experiments in vacuum, we have observed that ignition does take place. These experiments were done under constant evacuating conditions so that gaseous species could not accumulate around the propellant. Under these conditions, the occurrence of significant gas-phase reactions near the propellant surface, according to the gas-phase ignition theory, is possible only to a limited extent. The back diffusion of the reactive oxidiser decomposition species into the propellant surface as required by the heterogeneous ignition theory, is also out of question. Thus, the conditions required for the occurrence of gas-phase and heterogenous reactions are quite remote. The observation of ignition in vacuum further establishes that condensed-phase reactions are extremely important for propellant ignition. Since vacuum is not essential for most of the practical ignition conditions, the relative importance of gas-phase reaction cannot be ignored. However, the experiments and the analysis given in this paper (at atmospheric pressure) give sufficient evidence for the occurrence of condensed-phase reactions during the course of ignition and, therefore, the development of a sound analytical theory must take into consideration the condensed-phase contribution towards the overall ignition process.

Our ignition experiments in vacuum prove beyond doubt that condensed-phase reactions dominate during the ignition of the propellant and this is most relevant for developing a theory to understand the ignition phenomena in vacuum and at low temperature environments. Such a study has a practical application to give necessary information for the development of an optimum igniter for the upper stage motors.

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