

The Role of Boron in Thermal Decomposition of Ammonium Perchlorate

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ABSTRACT: Simultaneous thermal analysis (STA) method has been applied to study decomposition reactions of AP under a flowing nitrogen atmosphere and static air. Results obtained indicate that a phase transformation occurs prior to the decomposition reaction. Decomposition takes place exothermally in two stages, first stage of decomposition could be suppressed by the controlled heating programme. Addition of a small amount of boron lowered the temperature of the exotherm and increased the overall enthalpy of reactions.

KEY WORDS: Ammonium perchlorate, Thermal decomposition, Catalytic effects, Solid propellant, Thermal analysis

Ammonium perchlorate (AP) is widely used in solid composite propellants as an energetic material. AP constitute between 60 to 80 percent of propellant composition, therefore its thermal behaviour has a major influence in the combustion performance of the system [1-3]. Thermal decomposition of AP and the influence of metals, metal oxides and other additives have been thoroughly investigated [3-5].

Mayer et al.[6] attributed the premature reignition of solid propellant test motors to the first stage decomposition of AP and they examined a number of methods to suppress this reaction.

Vemeker et al. [7] published several reports on burning characteristics of AP propellants and their mechanisms by thermoanalytical methods [8]. In this study the simultaneous thermal analysis technique was applied to study AP decomposition and its reac-

tion with boron. Fine boron particles are usually added to solid propellants in order to increase combustion potentials such as burning rate and specific impulse [9]. In present study very fine boron particles were mixed with AP, their combustion reactions were studied by STA under predetermined conditions, and a comparison were made with the results on pure AP. STA allows monitoring of mass loss and energy changes in the sample simultaneously, enabling to compare these two parameters [10].

EXPERIMENTAL

Boron was supplied by Merck Co Ltd., with purity over 96% and the particle size of below 10 μ m. AP was received in crystalline form with 99.3% purity, it was ground to a particle size that passed through a 200 mesh.

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A simultaneous thermal analysis apparatus of PL Laboratories Ltd., model STA-1500 was used for measuring the weight loss and enthalpy changes of the samples as it was subjected to controlled conditions.

All experiments were carried out under the flowing nitrogen or static air, and for each experiment between 5 to 15 mg of sample was used.

AP-B compositions after mixing were compressed under 640 kgf/cm² pressing load to form a tablet and the STA samples were taken from the resulting tablets.

RESULTS AND DISCUSSIONS

Typical DTA and TGA curves are presented in Fig. 1. The results show that an endothermic valley appears at 232°C without weight loss, this has been assigned to the phase transformation of crystal structure from orthorhombic to the cubic [11]. The phase transformation is followed by decomposition reactions taking place at two stages. In DTA curves they are represented by two exothermic peaks maximizing at 282°C and 362°C respectively. The first stage of decomposition is accompanied with approximately 27% weight loss, the remaining AP reacts to completion in the second stage without any solid residue. Mayer et al. [6] considered the first exotherm as the source of premature enthalpy that can cause erratic combustions in propellants. They showed that this reaction could be suppressed by controlled heating.

In our STA studies a sample was programmed to be heated up to the end of the first exotherm then allowed to cool to below that of the phase trans-

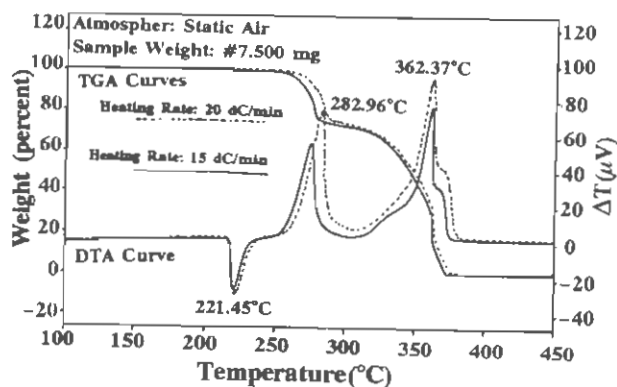


Fig. 1 : TGA and DTA traces of ammonium perchlorate

formation endotherm. Upon reheating this sample as shown on Fig. 2 and denoted by the dashed lines in DTA curves, the endothermic phase transformation reappeared indicating reversible phase transform. However the first exotherm does not appear as shown on Fig. 2 indicating that the reaction is irreversible and completely suppressed by controlled heating. Since the remaining AP from the first stage has a crystal structure as normal AP, the disappearance of the first exotherm must be due to reasons unrelated to the chemistry of the AP. Jacobs and Whitehead [12] found that the products of first stage of decomposition are mainly NH₃ and ClO₄H and they partly remain adsorbed on the porous residual crystals. Their findings were supported by the experiments on AP under pressurized NH₃ and ClO₄. The STA results confirmed the Jacobs and Whitehead's findings by showing a notable difference between mass loss and the energy change corresponding to the first exotherm. Weight loss was around 8% lower than the energy change.

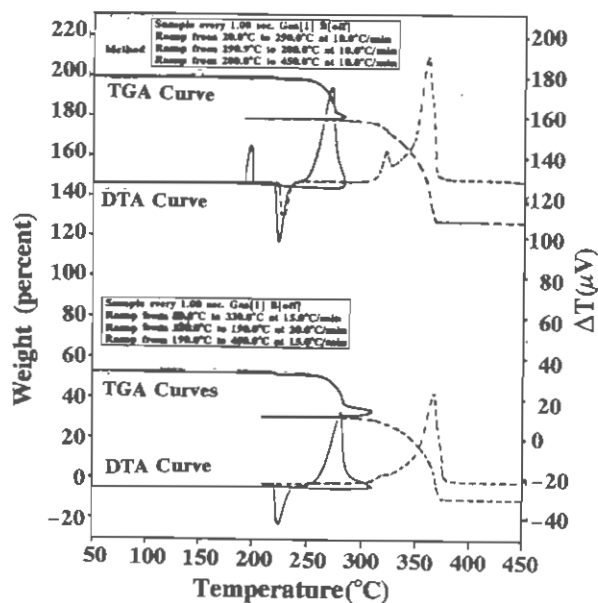


Fig. 2 : Multistep TGA and DTA traces of ammonium perchlorate

Catalytic Effects of Boron

Thermochemical properties of various AP/B mixtures were also examined by STA. Loose powder mixtures of AP with boron did not react. AP decom-

posed independently while boron remained unreacted however, the compressed AP/B mixtures showed enhanced reactivity. Rate of heating and sample weight were also influencing factors on the occurrence of the reaction. Fig. 3 shows that the endothermic phase transformation peak is not altered by the addition of boron. On the other hand the maximum decomposition reaction temperature was shifted to lower temperatures with the addition of boron. The effect was mainly on the second exotherm and there was no remarkable change in the first exothermic reaction. In summary the addition of boron lowered the temperature of exotherms, increased the total enthalpy and sensitized both peaks.

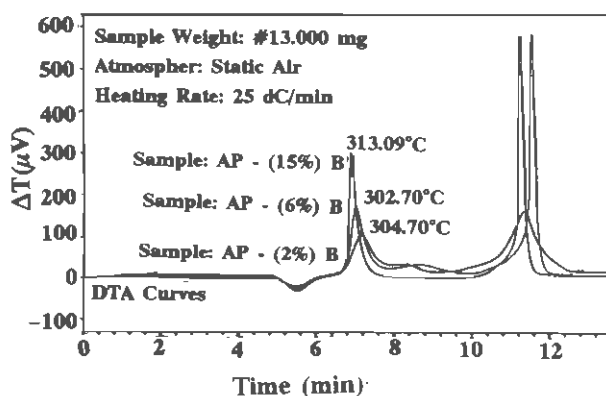


Fig. 3 : DTA traces of boron and ammonium perchlorate mixtures

CONCLUSIONS

Simultaneous DTA and TGA results revealed that in the first stage of decomposition of AP the weight loss is lower than the energy change, this confirms

the mechanism suggested by Jacobs. The remaining AP form the first stage has a crystal structure as normal AP. Addition of boron did not alter the first peak, but it sensitized both exotherms, lowered the temperature of reaction and increased the total enthalpy.

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