Study on Pyrolytic Mechanism of Composite Solid Propellant Based on Meso Hot Spot Model

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Abstract. The heat decompose mechanism of HTPB propellant was discussed in micro-structure. A meso-hotspot physical model was established combining chemical kinetics, heat transfer, and AP interface evolving. The proceeding of Heat Decompose of HTPB propellant was simulated. The results show that simulation results were consistent with experimental results. The nature of heat decompose processing of HTPB propellant was discovered.

1. Introduction
For solid propellants, the environmental conditions in the actual use process are quite complex. It is difficult to evaluate the safety of solid rocket propellants in one experiment. Generally, a variety of experimental methods are used to evaluate the safety of propellants. Because the cost of the experiment is high and the danger is great, especially for the prediction of ignition, on the other hand, it is very difficult to get the exact solution by the analytical method. Therefore, it is very important to calculate the criticality of the energetic material by the numerical method. Most of the current numerical research focuses on the simulation analysis of the macro structure safety, which can give a certain degree of variation of the internal temperature, time and space of propellant components, and thus analyze the location of the thermal ignition of propellant components. However, at present, the macroscopic analysis and modeling are coarser, the material model is complex, and the parameters are difficult to obtain. The simulation results can not directly guide the design of solid propellant materials. In this paper, through the establishment of solid propellant decomposition model structure of cellular heat of HTPB propellant pyrolysis for solid propellant formulation design to the slow cook off effect of thermal safety, provide effective means for supporting the propellant thermal safety design and evaluation.

2. Physical Model
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2.1. Basic Assumptions
As Al and additive components are less involved in chemical reactions during slow roasting and only mainly affect the thermal conductivity of adhesives, these components should be considered in the modeling of adhesives, and the microstructure modeling of HTPB propellant should mainly include AP particles, adhesives and AP-adhesives interfaces. Among them

Propellant mesoscopic chemical reactions are mainly the thermal decomposition of AP, dope thermal decomposition, AP the REDOX reaction of adhesive interface, including the thermal decomposition of AP will cause the AP internal gap formation, AP the evolution of the bonding
interface and the thermal conductivity performance degradation, and bonding agent in the process of slow heating, small deformation, thermal conductivity has some change.

Therefore, in order to facilitate the study of the problem, the following basic assumptions are made for the micro-combustion process of propellant based on the previous experiments:
1) All chemical reactions are one-way irreversible;
2) The heat transfer in each component of the propellant has only thermal conductivity, and the reaction products have no movement;
3) There is no material exchange in the reaction system, and the heat exchange at the boundary follows Newton's cooling law;
4) During the reaction, the mass and volume of AP will decrease due to the generation of internal voids and boundary evolution, and the volume of adhesive (including Al) will remain basically unchanged during the reaction.
5) There is no temperature difference between the two sides of the AP-adhesive interface at the beginning, and the thermal conductivity weakens with the evolution of the interface during the heating process;
6) The reaction substance is isotropic and has no phase transition.

2.2. AP Chemical Reaction Model
AP is the most commonly used oxidant in composite propellants, modified double-base propellants and NEPE propellants, generally accounting for more than 70% of the total propellants. It has the advantages of good compatibility, high gas production, low moisture absorption and low cost. AP is relatively stable at room temperature. From rhombic to cubic at 240°C, it absorbs water in moist air. When the pure AP is heated to 130°C, it begins to decompose, sublimes to 260°C, escapes brown vapor at 300°C, and burns at 400°C. The thermal decomposition process of AP is quite complex and greatly affected by decomposition conditions.

The thermal decomposition process of AP can be roughly divided into the following three steps: about 240~250°C is the crystal transformation process of AP, and AP reversibly transforms from the low temperature rhombic crystal to the high temperature cubic crystal. This process is an endothermic process; the low temperature decomposition stage of AP is about 350°C. The low temperature decomposition of AP is mainly a solid-gas polyphase reaction. At low temperature, perchloric acid is decomposed and oxidizing intermediate products ClO3, ClO, O2 and H2O are generated. Oxidizing intermediate products such as free O oxidize with part of NH3. This stage is an autocatalytic process. After a period of induction, the decomposition process gradually accelerates the reaction. After reaching the maximum value, the decomposition rate slows down again. As NH3 is not oxidized at low temperature will cover the activation center on the surface of AP crystal, the low temperature decomposition process stops. After decomposition, the remaining solids are still ammonium perchlorate, and the chemical properties do not change, but become relatively stable porous substances. The porous material can recover its low temperature activity by sublimation recrystallization or mechanical vibration. The low temperature decomposition process of AP is an exothermic process. About 350~460°C is the high-temperature decomposition stage of AP, which is the main decomposition stage. In this stage, AP is completely decomposed. But not autocatalytic type, no induction period. High-temperature decomposition first involves the proton transfer from NH4+ to ClO4-. Unlike low-temperature decomposition, the reaction occurs on the surface of AP. As the temperature continues to rise, due to the desorption of NH3 and partial liquefaction of AP, not only does HClO4 oxidize NH3 in the gas phase, but also the decomposition process of AP occurs on the surface of condensed phase. The oxidation reaction of NH3 by HClO4 and its degradation products is intensified, and exothermic decomposition is obviously dominant.

The thermal decomposition process of AP can be described by a simplified three-step, four-component chain chemical reaction model.

2.3. Chemical Reaction Model of Adhesive Matrix
Compared with AP, the heat release from thermal decomposition of adhesives is relatively small, and its influence on thermal decomposition is mainly reflected in its influence on thermal conductivity and
catalysis of chemical reaction of AP. In this stage, the research mainly considers the influence of chemical reaction and thermal conductivity of adhesives.

It is assumed that the adhesive chemical reaction model is simplified to a three-component two-step chemical reaction.

2.4. Boundary and AP-adhesive Motion Interface Model
The cell boundary is the first kind of boundary condition, that is, the cell temperature on the boundary is equal to the ambient temperature $T_e$.

Assuming that the AP-adhesive chemical reaction interface is a thin layer with a very small thickness, the thermal coupling boundary condition is used to describe the interface. At the beginning, the AP interface temperature is equal to the interface temperature $T_b$ of the adhesive.

The contact thermal resistance gradually increases with the evolution of AP interface. The following calculation formula is adopted to approximate the change of thermal resistance

$$ R_{AP-B} = R_0 (d_0 - d_t)/d_0 $$

(1)

3. Micronumerical Simulation of Propellant
In Figure 1, respectively gives the heating rate of 5 ℃ / min, the temperature distribution of different time and AP evolution, from figure can be seen, when the temperature of the AP to chemical exothermic reaction temperature, the thermal conductivity is low, because of the HTPB AP fever, and can not be AP core temperature significantly higher than the boundary temperature, namely: the HTPB adiabatic effect makes the boundary temperature relative to the AP exothermic peak will ahead of time.

![Temperature Cloud](image)

**Figure 1.** A temperature cloud with a volume fraction of 0.5

Different AP content (70% and 50%) slow roasted mesoscopic simulation of combustion process mean TG curve is shown in Figure 2, can be seen from the diagram, the AP content high propellant decomposition peak temperature is relatively low levels of delay, the average delay about 7 ℃ low temperature decomposition peak temperature, high temperature decomposition peak delay about 4 ℃, analysis its reason, mainly because with the increase of the content of HTPB propellant material to the AP decomposition exothermic heat conduction ability relative decline, especially for the low temperature stage, thermal capacity is relatively smaller, the heat generated in the decomposition of
AP can’t timely send out through the matrix, the AP core temperature the average temperature is higher.

![Graph](image)

**Figure 2.** Thermal decomposition DSC-TG curve of HTPB/AP system

### 4. Conclusion
Hot butyl hydroxy propellant of mesoscopic physics model is established, considering the solid propellant component chemical reaction heat, heat conduction and AP interface evolution effect on the properties of solid propellant material thermal safety, through calculation can get different material such as AP volume fraction and the content of Al design influence on thermal safety, get the propellant thermal decomposition mesoscopic structure and evolution law of temperature field for direct heat propellant material design and structural safety assessment provides the basis.

### 5. References

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