

Investigation of heat transfer and heterogeneous reactions during the Slow Cook Off of a composite Propellant

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1 Introduction

The use of aluminum/ammonium perchlorate/HTPB propellant is common and is normally well known. However some accidents occur when such substances are slowly heated. In this context of Slow Cook Off, the thermal decomposition of ammonium perchlorate has been extensively studied in the past. The process of decomposition of this compound plays a great role in hazard explosion [1]. However the presence of other components (binder, aluminum, catalyst) has also to be considered.

Although these propellants are heterogeneous, most of the models of self ignition published in open literature [2] are based upon two homogeneous phases (gas and solid). More over the interaction of products of decomposition of AP and HTPB are not elucidated. The influence of pressure, during self heating, is not clearly described.

Nevertheless, the various results published illustrate, on the one hand, significant differences regarding the influence of different parameters on the decomposition and on the other hand, a lack of useful quantitative laws to predict the thermal behavior of the element under a range of conditions (temperature, duration of exposure, presence of containment).

The investigations carried out in previous studies enabled us to identify a mechanism of thermal decomposition of ammonium perchlorate in the field known as of the “low temperatures” (150-250 °C).

With the aid of a set of experimental devices not always available in past studies (TG/MS, SEM, FTIR), the purpose of this paper is to both clarify the difference observed in the literature in order to understand the detailed decomposition heterogeneous kinetic process of ammonium perchlorate and to establish analytical laws to facilitate the prediction of the thermal behavior of ammonium perchlorate.

The aim of this work is to build a new modeling of the above aspect interaction during self heating of such propellant. The phenomenon was previously described by experimental approaches [3-4]). Heat and mass balance will be considered both in solids and gas phase.

2 Principle of modeling

A large experimental study [3] was led on the behaviour of five composite propellants subjected to slow heating like on their principal components: the ammonium perchlorate and polybutadiene. In order to improve the description of the thermal damage mechanism of those propellants, two complementary approaches were carried out. First of all, a morphological approach enabled us to analyze, in detail, the evolutions of the microstructure of propellant and its components during the phase of heating.

The whole set of observations informed us about the various stages of the process of decomposition of the mixtures. Time and temperature of exposure are key parameters of the process of thermal decomposition. From the systematic analysis of image carried out, on ammonium perchlorate and propellant, it is possible to describe the chronology of the process and the influence of the interactions between compounds as follow:

- The partial thermal decomposition of the binder begins but the binder preserves a good behavior and continues to play its part of matrix in bearing the ammonium perchlorate loading.
- The decomposition of the binder continues, the binder has a more granular structure now and sometimes streaked.
- The decomposition of ammonium perchlorate begins, porosities appear inside grains and a more marked decomposition of the binder appears, a strong decoherence occurs, (having probably for origin the modifications of the binder caused by the oxidation of the chains of polymer by the products of decomposition of ammonium perchlorate [5]).
- The partial decomposition of ammonium perchlorate occurs on large arrays of sample.

The thermal damage of these propellants thus takes the form of porosities of two types: intra granular porosities in ammonium perchlorate grains and extra granular porosities.

An analysis of surfaces, by infrared spectroscopy, of the heated crystals highlights a process of decomposition in volume of ammonium perchlorate with like first stage a reaction in solid phase followed by diffusion of species towards the surface. This diffusion is combined with diffusion of gaps coming from surface towards the centre of the crystals thus explaining the initial appearance of porosities towards surface. A series of experiments, obtained with a specific device, made it possible to highlight the effect of containment on the decomposition of AN particles. The proximity of products of decomposition of ammonium perchlorate causes to inhibit the thermal decomposition of this last. The stage of decomposition of ammonium perchlorate following the phase of volume diffusion is thus a surface reaction involving reactions of adsorption and desorption.

A gas analysis, by mass spectrometry, made it possible to identify like products resulting from the thermal decomposition of ammonium perchlorate the following products: H_2 , N_2 , O_2 , Cl_2 , O , NO and NO_2 .

The systematic analyzes in DSC and TGA on composite propellants made it possible to evaluate the influence of the various components of the composite propellants as well as the influence of various parameters like the surrounding atmosphere. It appeared that the decomposition of the binder polybutadiene was sensitive to the surrounding atmosphere and more particularly to the presence of oxygen which, in addition, is a product of decomposition of ammonium perchlorate. The whole of these results enables us to propose a physical model multi decomposition of composite propellants. The decomposition of ammonium perchlorate and HTPB binder is summarized in figure 1. Furthermore, our experimental study allow us to quantify a large number of parameters of the modelling (kinetic parameters, energy, reaction rates) and analytical laws describing influence of time, temperature, particle size and containment on the decomposition.

This extensive characterization allows building an heterogeneous kinetic model of degradation of the propellant. This modelling is composed of 95 equations describing, for each phases, energy and mass transfer. Reactions Adsorption desorption of products of decomposition have been taken into account for each AP particle. The second step of the work consisted in implementing this model in COMSOL environment and in verifying its behaviour for a whole set of boundary conditions. The model is modular and allows the integration of new laws to take into account other compositions.

3 Numerical results

Figure 2 presents the mass loss of AP, HTPB, a propellant (82 wt% AP, 18 wt% HTPB) and a virtual propellant obtained by combination of decomposition curves of AP and HTPB affected by coefficients 0,82 and 0,18. Presence of O_2 , NO , H_2O and NH_3 in the decomposition process of AP and HTPB explain why decomposition of an AP/HTPB based propellant (propellant A) is not only the superposition of the decomposition of AP and HTPB. They are strong interactions between decomposition products of AP and HTPB and decomposition products of HTPB and AP.

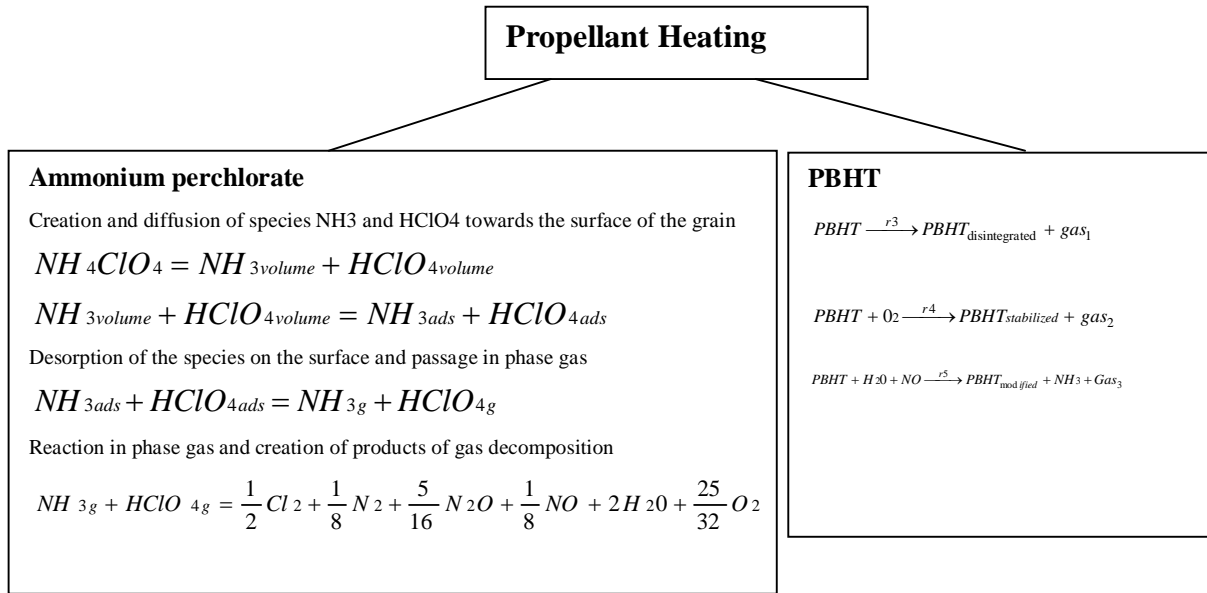


Figure 1 : Thermal decomposition mechanism of an AP/HTPB based propellant

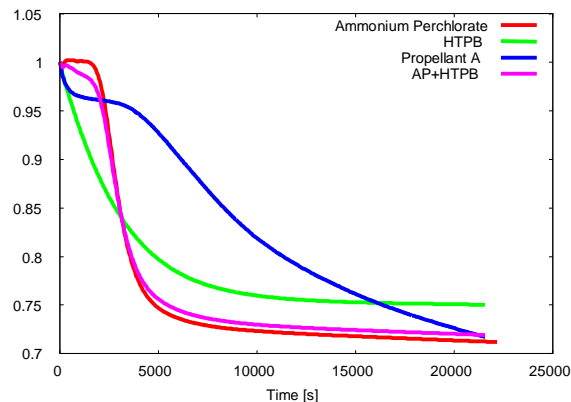


Figure 2 : Comparison of mass loss of AP, HTPB, virtual propellant, real propellant ($T= 226\text{ }^{\circ}\text{C}$ under Argon)

The complete interaction was tested with 7 AN particles surrounded by HTPB binder which is in contact with gaseous ambient medium. By an integration of concentration decrease of each reactive particle in the whole array of AN and binder, it is possible to obtain the mass at each time. Thus it is possible to draw the mass loss versus time for a given temperature and compare with an experiments performed in the laboratory in the same conditions. The result of comparison is presented in figure 4. It appears that in first stage of decomposition a large deviation occurs between experimental curve and numerical modelling, but the agreement is better after 3000 s.

This is a first trial for a new approach in thermal decomposition of composite propellant and it is now expected to increase the size of virtual pellet of mixture in order to reach more realistic values. More over a better kinetic law for germination growth initial step should allow us to improve the agreement between the first stages of thermal decomposition. The growth of inside porosity should allow a comparison with experimental observations.

References

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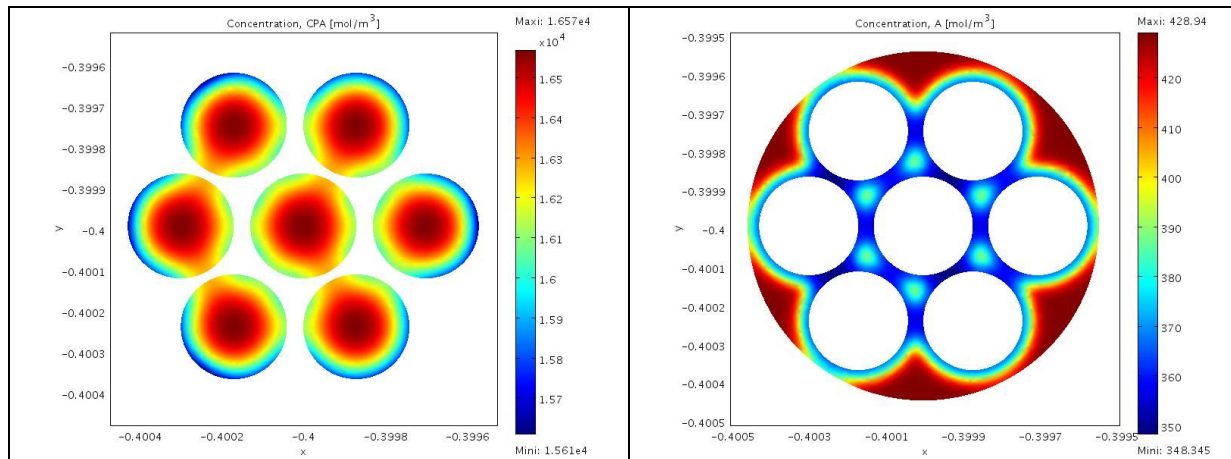


Figure 3: View of AN concentrations (left) and HTPB concentrations (right) after heating during 1000 s at $T = 226\text{ }^{\circ}\text{C}$ under Ar.

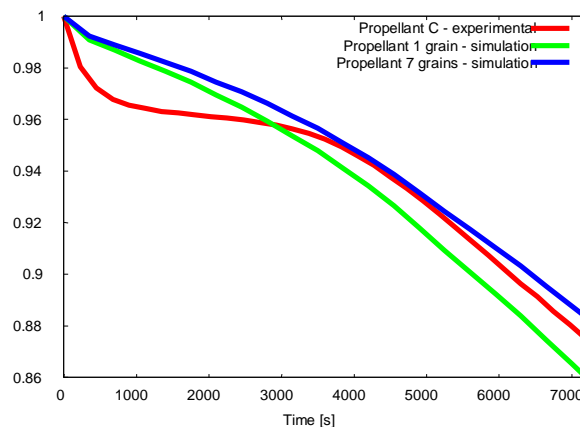


Figure 4: Comparison of mass loss with TGA experiments and numerical modelling matching with the configuration presented in figure 3.