

FLAME STRUCTURE OF SANDWICH SYSTEMS BASED ON AMMONIUM PERCHLORATE, HMX AND POLYBUTADIENE RUBBER STUDIED BY PROBE MASS-SPECTROMETRY AND MODELING.

A.A. Chernov, V.M. Shvartsberg, N.E. Ermolin, O.P. Korobeinichev, V.M. Fomin
Institute of Chemical Kinetics and Combustion
Siberian Branch Russia Academy of Science,
630090 Novosibirsk, Russia

Keywords: chemistry of combustion, solid propellant, mass-spectrometry, modeling

ABSTRACT

The structure of subatmospheric flames of sandwich-type systems consisting of alternating laminae of ammonium perchlorate (AP) or HMX and "base" (polymerized mixture of fine-grained AP and polybutadiene binder) has been studied. The burning surface shape as well as the profiles of concentrations for 17 stable components and of temperature for three crosssections corresponding to the middle of "base" lamina, and to the interface between the laminae have been determined. The hypothesis assuming the existence of three types of flames in sandwiches has been verified experimentally. A concentration gradient of fuel components has been observed at the burning surface of the oxidizer, directed towards the burning surface. Multizone structures and step-by-step mechanisms of reactions in AP and HMX flames have been confirmed. A numerical study for the flame structure of sandwich system based on AP and "base" have been carried out. A simplified set of equations obtained from a complete Navier-Stokes set with the limiting transition $M \rightarrow 0$ have been used in order to construct a solution. Satisfactory agreement between calculated and experimental data on flame structure have been obtained.

INTRODUCTION

An important role in the combustion process for mixed solid fuel (MSF) is played by microflames caused by heterogeneous distribution of the oxidizing agent in the fuel-binder. The dependence of combustion rate on particle fineness and the effect of microflames on the formation of local thermal and diffusion flows point to the necessity of studying the local structure of flames. MSF consist of coarse-grained AP (particle size several hundred micrometers), the space between the particles being filled with the "base" - the mixture composed of a fuel-binder and fine-grained AP (particle size from a few micrometers to a few tens of micrometers). Therefore, oxidizer - "base" sandwiches should be the best models for composite systems. Such sandwiches, however, have been considered only by Price and co workers / 1 /. The other studies performed hitherto dealt with sandwiches consisting of alternating laminae of oxidizer and fuel - binder. There are no published works on combustion of HMX - based sandwiches. The aim of this work was to study chemical and thermal structure of flame for sandwiches on the basis of AP or HMX and the "base" consisting of AP (<50 mkm) and carboxy terminated polibutadiene (CTPB).

EXPERIMENTAL

The sandwiches consisted as a rule of five alternating laminae: three AP (or HMX) laminae and two "base" laminae. An AP-based (system 1) was made of pressed AP plates (density 1.85 g/cm³, thickness 1.3 mm) and the laminae (thickness 1.0 mm) of polymer "base" - the mixture of fine - grained AP (particle size < 50 mkm) and CTPB in a 4:3 ratio. The mixed "base" laminae were prepared by polymerization in Teflon arrays at 100 °C for 24 hours. The sandwich samples were 4.8*6*10 mm. An HMX-based sandwich (system 2) was made of 1 mm thick HMX laminae (mixture of fine-grained AP and CTPB in a 73:27 ratio). The sandwich dimensions were 4.2*6*12 mm.

Thermal structure of the flames was studied using thermocouples (tungsten-rhenium wires 30 and 50 mkm in diameter) embedded in propellant samples. Chemical structure of flame was analyzed by mass-spectrometric probing described elsewhere (2). Quartz cones: 15-20 mkm sampling orifice, 0.45 for system 1 and 0.15 for system 2 external tip diameters, 40-50 grad. interior angular openings. Systems 1 and 2 were examined in helium flow at pressures of 0.03 MPa and 0.053 MPa, burning rates 0.3 mm/s and 0.65 mm/s, respectively. In order to study the structure of burning surface and the shape of oxidizer and "base" laminae, the samples were quenched using rapid depressurization. At low pressures AP-lamina and HMX-lamina protrudes above "base" lamina approximately by 0.5 lamina thickness and has the shape close to a circle segment. At 4 MPa the "base" and AP laminae have similar V-shaped profiles.

SET OF EQUATIONS. METHOD OF SOLUTION

Flow at a MSF combustion surface is defined by Mach numbers of <0.003 and Reynolds numbers of $10-200$. A simplified set of equations obtained from a complete Navier-Stokes set with the limiting transition $M \rightarrow 0$ have been used in order to construct a solution. Thermal and diffusion flows are specified in accordance with (3). In (3). In the present studies in order to construct a solution a splitting method (4) combined with the method of artificial compressibility is used. On the basis of the calculations performed (5) a kinetic mechanism including 58 elementary stages and 35 components is separated.

RESULTS

The following components have been found out in the sandwich flames: H_2 , NH_3 , H_2O , C_2H_2 , HCN , CO , N_2 , NO , HCl , CO_2 , N_2O , NO_2 , $CLOH$, O_2 , C_2H_6 , ClO_2 , Cl_2 , $HClO_4$, whose mole fractions and temperature profiles are shown in figs. 1-2. Analysis of the data obtained testifies to the fact that there are two zones in the flame of sandwich-type system 1 in the cross section corresponding to the middle of AP lamina (fig.1a). The first zone adjoining the burning surface of AP is a narrow (about 0.2 mm) AP flame zone wherein ammonia is oxidized by $HClO_4$ and ClO_2 to yield NO , O_2 , and other substances. In the second, more wide (about 3 mm) zone, O_2 and NO are consumed. Oxygen and nitric oxide are consumed in oxidation reaction of carbon monoxide with CO_2 and N_2 formation; HCN , C_2H_2 and H_2 are oxidized slowly. The experiments have shown that at the distances from sample surface longer than 5 mm CO and N_2 concentrations do not change. It should be noted that the fuel components, i.e. products of "base" destruction, HCN and C_2H_2 , penetrated right up to the oxidizer surface due to diffusion: there is a concentration gradient of the components, directed to the burning surface. These products can react with AP, that may be an additional source of heat release on the burning surface. On the other hand, the probability of such an interaction is confirmed by the work reported by Inami et al. (6), wherein AP decomposition in the presence of gaseous propylene has been studied.

Data on flame structure for system 1 in the crosssection corresponding to the middle of a "base" lamina (fig.1b) also indicate that there are two zones: a narrow (0.3 mm) zone of the oxidation of butadiene (fuel-binder destruction product) by ClO_2 and $HClO_4$ with formation of carbon monoxide and other substances and a wide (2-3mm) zone of consumption of ammonia, carbon monoxide, $HClO$ and accumulation of other substances due to their diffusion from the oxidizer lamina. Inhibition of ammonia oxidation in the presence of butadiene is observed.

Fig.2a shows profiles of mole fractions and temperature in flame of sandwich system 2 in the cross section corresponding to the middle of an HMX lamina. Chemical structure of the flame in this cross section is identical to the chemical structure of pure HMX flame at 0.1 MPa (7). Two zones may be distinguished. The first one is a narrow (of 0.2-0.3 mm width) zone of NO_2 and CH_2O consumption and accumulation of nitric oxide and other substances. The second, more wide (2-3 mm), zone is that of the oxidation of cyanic hydrogen by nitric oxide. As shown by Cohen et al. (8), the reaction of HCN with NO plays the principal role in the high temperature zone of HMX flame. The circularity of laminar system flame (HMX lamina) lies in the fact that cyanic hydrogen is oxidized by nitric oxide incompletely. This may be accounted for by thermal interaction between the laminae. The flame of HMX lamina transfers some heat of "base" flame, the temperature decreases (as compared to adiabatic temperature for HMX), and the rate of the $HCN + NO$ reaction decreases. On the other hand, HMX lamina in the condensed phase receives a portion of the "base" lamina heat and HMX becomes able to burn steadily at 0.053 MPa (at this pressure pure HMX burns unsteadily). The data obtained on HMX flame structure confirm the mechanism adopted by Bizot et al. (9) in the model for HMX combustion and are consistent with data reported by Kubota and co workers (10). The main reaction in the zone adjacent to the HMX burning surface and responsible for the heat transfer to the condensed phase is seemingly the reaction between NO_2 and CH_2O and not the decomposition reaction of HMX vapors, as it was assumed earlier (8, 11).

RESULTS OF CALCULATION

Fig 3 shows results of computer simulation of AP-based sandwich flame (system 1) at 0.03 MPa: profiles of mole fractions H_2 , HCN , C_2H_2 , the shape of combustion surface between the central layer AP ($Z=1.2$) and the central layer "base" ($Z=0$) together with field of velocity (standardized to 1.5 m/sec), the isoline of HCN concentration and temperature. Calculations were carried out for plane-parallel and asymmetric flows on curvilinear grids with a number of nodes 20×20 , condensed in regions of higher gradients. Blowing mixture from the combustion surface takes a direction on the normal to the surface. At the combustion surface depending on the pressure, the values of temperature, rate, and molar fractions of components A_i are prescribed. At low pressures A_i corresponds to the experiment, and at high pressures to rough extrapolation of data for combustion of AP and a layered system. At the lower and upper boundary of the calculation region conditions are prescribed, and at the outlet conditions are extrapolated. The temperature of the combustion surface in calculations is prescribed by the

relationship $T=673 + 30 \times (1 + \cos(\pi(1 - Z/1.2)))$ and it equals the experimental temperature with $Z=0$ and $Z=1.2$ mm. In both calculations and the experiment a broad mixing layer is observed washing the combustion surface, although there is no total mixing in the region with right-hand boundary $X=3$ mm. The reaction occurs in kinetic region, and the temperature field in sections $X = \text{const}$ (see Fig.3) levels out the concentration fields more intensely. Good agreement of calculations and the experiment is observed. The value for thermal flow over normal to the combustion surface is provided below (W/m^2): 1×10^5 ($Z=1.2$), 2×10^5 ($Z=0.55$), 3×10^5 ($Z=0$). The ratio of this flow to similar flow for a plane combustion surface reaches a maximum value of 2.4 at $Z=1.2$ mm. At high pressures the difference in thermal flows of the combustion for plane -parallel and asymmetries flows does not exceed 3%. The point with the maximum value of thermal flow shifts in the direction of oxidizing agent.

REFERENCES

1. Price E.W., Sambamurthi J.K. et al., Comb. and Flame, 63, 381 (1986).
2. Ermolin N.E., Korobeinichev O.P., Tereschenco A.G., Fomin V.M., Comb., Explos. and Shock Waves, 1, 18, 36 (1982).
3. Ermolin N.E., Korobeinichev O.P., et al., Khim. Fiz., N12, p.1711(1982).
4. Kovenya V.M. and Yanenko N.N., The Spilting Method in Problems of Gas Dynamics (in Russian), Nauka, Novosibirsk (1981).
5. Korobeinichev O.P., Chemov A.A., et al., Fiz. Gorenia Vzryva, 26, 3, 46(1990)
6. Inami S.H., Ragapakse Y.H., Wise H. Comb. and Flame, 17, 189 (1971)
7. Korobeinichev O.P., et al., Comb. Explos. and Schock Waves, 20, 3, 282(1984).
8. Cohen N.S., Lo G.A., Crowley L.H. AIAA-Journal, 23, 2, 276 (1985).
9. Bizot A., Bekstead W.M.. A model for HMX propellant combustion. Paper at the 3-rd Int. Seminar of Flame Structure, Alma-Ata, 1989.
10. Kubota N., Sakamoto S., Propellants, Explosives, Pyrotechnics, 14, 6(1989).
11. Ben-Reuven M., Caveny L.H. AIAA-Journal, 19, 10, 1276 (1981).

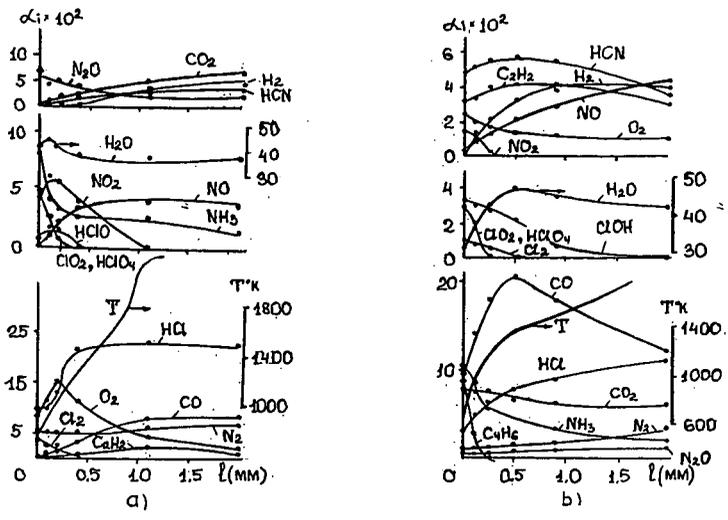


Fig.1. Mole fractions of combustion products and temperature profiles in the AP-based sandwich (system 1) flame obtained by mass-spectrometry probing in the transection corresponding the middle of : a) AP-lamina b) "base" lamina

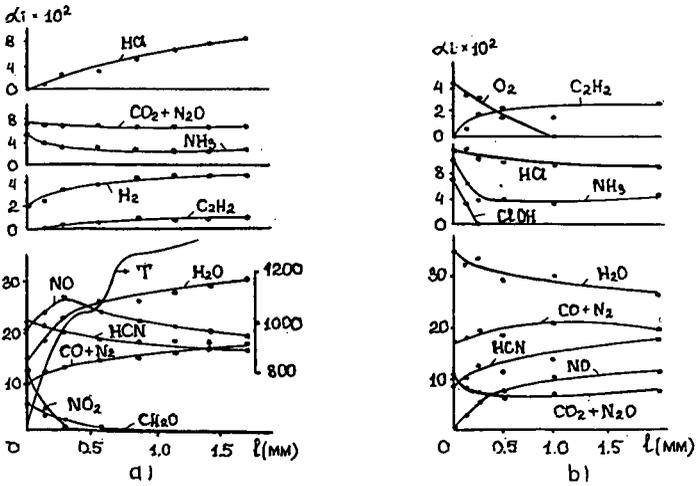


Fig.2. Experimental data of probing HMX-based sandwich flame : a) HMX lamina , b) "base" lamina

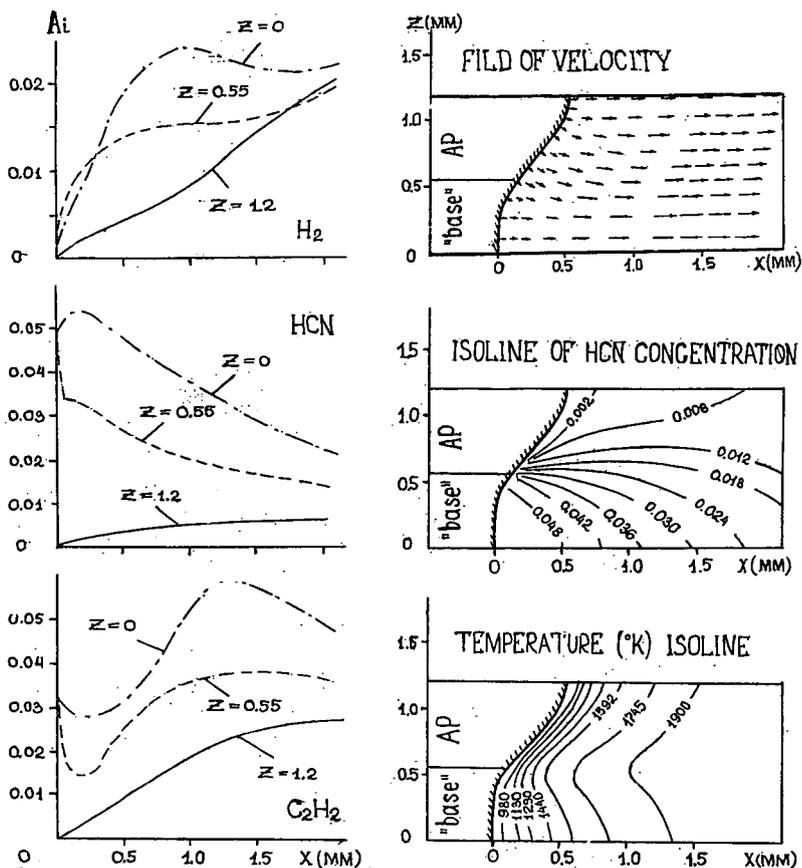


Fig. 3. Results of computer simulation of AP-based sandwich flame (system 1) at $P=0.03$ MPa