

Combustion characterization of hydrazinium nitrate/energetic binder/Alex based model propellants

Vladimir E. Zarko^{a,*}, Vladimir N. Simonenko^a,
Gennady I. Anisiforov^b, Alexey V. Aparin^b

^a Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia

^b Boreskov Institute of Catalysis, Novosibirsk 630090, Russia

Received 25 January 2006; received in revised form 18 July 2006; accepted 24 July 2006

Available online 6 December 2006

Abstract

The hydrazinium nitrate ($N_2H_4 \cdot HNO_3 - HN$) can be considered as a candidate for using instead of ammonium perchlorate (AP) in eco-friendly solid propellant formulations. In combination with energetic binder it provides reasonably high energetic parameters of solid propellant. In addition, the substitution of AP by HN leads to decrease in the combustion temperature. The combustion of the HN based metallized propellants containing energetic binder has been investigated. The effect of partial substitution of commercial Al powder by Alex on the propellant combustion characteristics has been examined. The burning law was measured in the pressure range 20–80 atm, the ignition delay time and temperature profile were measured at atmospheric pressure. Some qualitative observations on the combustion behavior of the propellants under study have been made by analyzing the video camera and recoil force transducer records.

© 2006 Elsevier Masson SAS. All rights reserved.

Keywords: Hydrazinium nitrate; Propellant; Burning law

1. Introduction

The hydrazinium nitrate ($N_2H_4 \cdot HNO_3 - HN$) is considered as a potential candidate for the replacement of ammonium perchlorate (AP) in solid propellant formulations. This oxidizer provides reasonably high energetic parameters of solid propellant, especially in formulations containing energetic binder. The results of preliminary calculations are shown in Table 1.

It is seen that substitution of AP by HN gives gain in I_{sp} value about 10 s. Note that this substitution also leads to decrease in the combustion temperature as well as in the mean molecular mass of the combustion products. The calculations were performed for formulations containing 15% by mass of HTPB. Theoretically, the higher specific impulse values (up to 271 s) can also be obtained if one analyzes formulations

Table 1

Thermodynamic parameters of the combustion products calculated for the expansion ratio 70/1 (atm)

EB	24	24	–	–
HTPB	–	–	15	15
Al	18	18	18	18
HN	58	–	67	–
AP	–	58	–	67
T (°C)	3488	3855	2692	3298
MM	17.7	22.6	14.3	18.7
I_{sp} (s)	273.1	262.3	260.9	264.8

containing 7–8% of inert binder (HTPB). However, such propellants could not be manufactured and are practically useless.

The experimental data on the decomposition and combustion characteristics of HN and HN based solid propellants are very restricted [3,4,8]. Recently, the data were reported [6] on the combustion characteristics of the model propellants, which contained AP, Al and inert binder HTPB. It has to be noted that the neat HN is a relatively “weak” monopropellant, which does not burn under pressures below 40 atm. It was found [6] that melted

* Corresponding author. Tel.: +7 383 3332292; fax: +7 383 3307350.
E-mail address: zarko@kinetics.nsc.ru (V.E. Zarko).

samples of neat HN with relatively small diameter (5 mm) did not burn in the pressure range 10–80 atm while 8 mm-diameter melted samples did not burn in the pressure range 10–60 atm and burned in unstable mode at pressures higher than 80 atm. At the same time the 8 mm diameter pressed samples of neat HN readily burned in self-sustaining regime under pressures 40–100 atm. In this pressure range the burning law for pressed (up to 95% of theoretical density) neat HN was the following: $r_b = \text{const } P^{0.76}$.

Addition of Ir containing catalysts led to drastic increase in the reactivity of pressed samples of neat HN. The catalysts were used in the form of thin Ir layer deposited on the surface of $\gamma\text{-Al}_2\text{O}_3$ particles. The mass content of Ir in catalyst comprised 10% or 30%. When doped with 0.5–1.0% (Ir containing) catalyst, the pressed samples of HN started decomposing exothermally and self-ignited in air several minutes after pressing. With 0.1% of catalyst the samples partially decomposed with increase in the sample original volume but self-ignition was not observed. Addition of 4% of catalyst, containing complex oxide of Cr and Cu, increased the burning rate of neat HN pressed samples by 2–3 times and decreased the pressure exponent up to the value ~ 0.33 .

It was shown experimentally [6] that non-catalyzed model propellants 85% HN/15% HTPB or 67% HN/18% Al/15% HTPB did not burn at pressures up to 100 atm. However, partial replacement of Al by Alex (electrically exploded Al with 100 nm nominal particle size) in the above formulations resulted in self-sustaining combustion in the pressure range 20–100 atm. The same occurred if the metal oxide catalysts were added into the model propellants based on HN and HTPB.

The goal of this study was to investigate the combustion of HN based propellants containing energetic binder. It was expected that such propellants may exhibit self-sustaining combustion modes in a rather wide pressure range. In addition, it was of interest to study the effect of partial substitution of commercial Al powder by Alex on the combustion characteristics of propellants under investigation.

The ignition delay and temperature profile have been measured at atmospheric pressure; the burning rate has been measured in the pressure range 40–80 atm. In addition, some qualitative observations on the combustion behavior of the propellants under study were made with video camera and use of the recoil force transducer.

2. Experimental procedure

The crystals of HN were synthesized by means of reaction between $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and concentrated HNO_3 . The reaction product was slowly evaporated at the temperature of 40–50 °C that resulted in formation of large size (10–15 mm) HN β -form crystals. The crystals were manually grinded and less than 63 μm fraction was used for manufacturing solid propellant samples. The characteristic sizes of HN particles were $D_{10} = 7 \mu\text{m}$ and $D_{30} = 24 \mu\text{m}$. The melting point of the crystals used was 71 °C and the decomposition starting temperature comprised ~ 180 °C. The combustion experiments were performed with uncured cylindrical propellant samples of 10 mm

length and 10 mm in diameter, which were tightly inserted into the plexiglass or quartz holders.

Ignition of the propellant samples at atmospheric pressure was performed by the radiant flux generated by powerful (5 kW) Xe-lamp. Ignition at elevated pressures was performed by the hot electrical wire. The temperature profiles in the combustion wave at atmospheric pressure were measured by the W/Re thermocouples made of 50 μm and 10 μm diameter wires. The size of the thermocouple bead was practically equal to the wire diameter. The burning rate under elevated pressures was measured in the strand burner via processing the pressure records.

The basic propellant formulation (P_1) contained by mass 58% of HN, 18% of commercial Al with 5 μm particle mean size, and 24% of energetic binder (polyvinyl tetrazole polymer plasticized with nitroesters, oxygen balance -53% , $\Delta H_f = -746 \text{ J/g}$). The modified propellant (P_2) had practically the same formulation but half of the commercial Al powder was replaced by nano-sized Alex. The characteristic sizes of commercial Al particles were $D_{10} = 3.3 \mu\text{m}$ and $D_{43} = 5.4 \mu\text{m}$ while the particles of Alex were less carefully characterized and had estimated mean size 0.1 μm .

3. Experimental results

The ignition delay time at atmospheric pressure under action of the radiant flux $62 \text{ J/cm}^2 \text{ s}$ was found to be equal to 0.6 s for P_1 and 0.4 s for P_2 propellants, respectively. The burning rate at atmospheric pressure comprised 0.85 mm/s and 1.05 mm/s for P_1 and P_2 propellants, respectively. The recoil force signal contained relatively large amplitude oscillations with frequencies 2–4 Hz for P_1 and smaller amplitude oscillations with frequencies 10–20 Hz for P_2 propellants, correspondingly.

Typical temperature profiles recorded by the W/Re thermocouples (50 μm diameter) are shown in Fig. 1 for the propellants P_1 and P_2 .

The burning rate–pressure dependencies for the propellants P_1 and P_2 are shown in Fig. 2. Rough approximations of the burning law are the following.

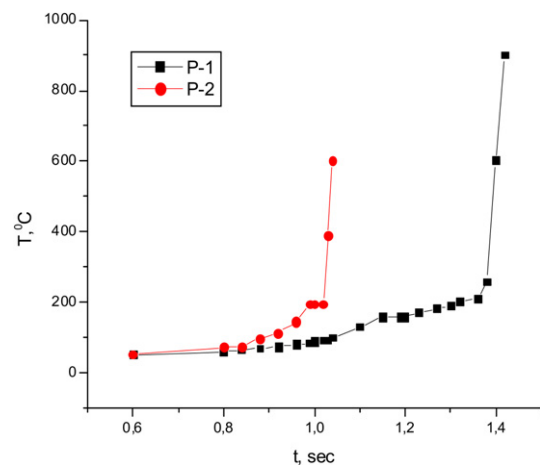


Fig. 1. Temperature distribution ($P = 1 \text{ atm}$) in the vicinity of the burning surface of the propellants P_1 and P_2 .

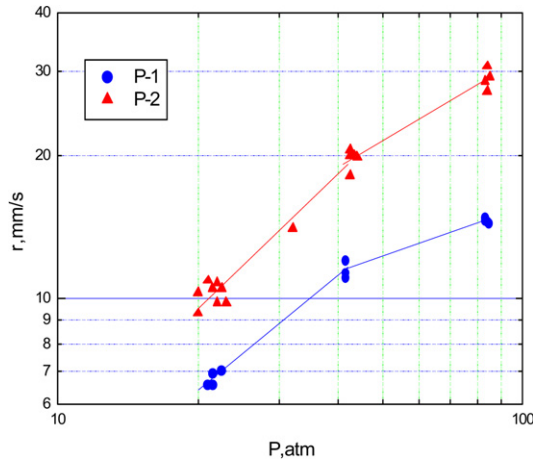


Fig. 2. Pressure dependencies of the burning rate for the propellants P_1 and P_2 .

In the pressure range 20–40 atm:

$$r_b \text{ (mm/s)} = 0.57P^{0.80} \text{ (atm)} \sim \text{Propellant } P_1$$

$$r_b \text{ (mm/s)} = 0.55P^{0.95} \text{ (atm)} \sim \text{Propellant } P_2$$

In the pressure range 40–80 atm:

$$r_b \text{ (mm/s)} = 3.2P^{0.34} \text{ (atm)} \sim \text{Propellant } P_1$$

$$r_b \text{ (mm/s)} = 2.3P^{0.57} \text{ (atm)} \sim \text{Propellant } P_2$$

4. Discussion

When starting discussion of available experimental data, one may recognize the essentially wider pressure range of self-sustaining combustion for HN/energetic binder propellants as compared with HN/HTPB ones. The thermocouple records exhibit some peculiarities in the temperature profiles recorded at atmospheric pressure. The important features of experimental temperature profiles are the extended plateau-like zone recorded in the subsurface preheat layer and surprisingly low (ca. 200 °C) magnitude of the burning surface temperature. These results have some preliminary character and can be corrected in the future after more detailed experimenting. Note that this information was obtained in experiments with uncured propellants. However, it has to be mentioned that extended preheat zone in the condensed phase has already been observed in combustion experiments with neat RDX and HNF [5,7], which both have relatively low melting point. A plausible reason for existence of extended preheat zone can be changing of thermo physical properties of the condensed substance due to formation of the gas bubbles in decomposing energetic material.

As for the relatively low burning surface temperature, it has to be mentioned that in the combustion of DINA (dinitroxydietylnitramine) at atmospheric pressure the burning surface temperature was found to be equal to 230 °C [1] and the temperature record contained small peaks presumably caused by the presence of bubbles in relatively thick preheat zone in the melted condensed phase. Low magnitude of the burning surface temperature correlates with the beginning of decomposition reactions in HN. It is supposed that the first step of the HN

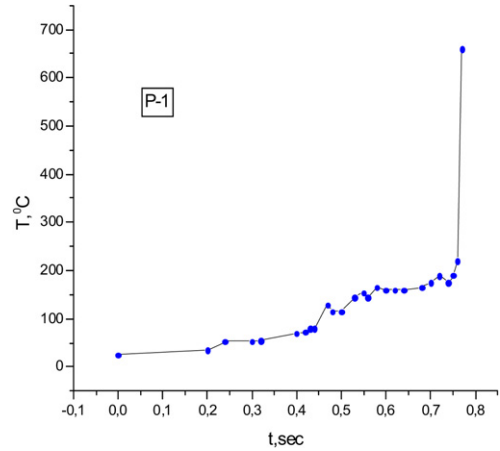


Fig. 3. Temperature profile recorded at $P = 1$ atm by 10 μm W/Re thermocouple in the propellant P_1 combustion wave.

reaction in a melted layer corresponds to its dissociation on hydrazine and nitric acid, which have the boiling temperature at atmospheric pressure equal to 114 °C and 84 °C, correspondingly. As was stated in [3], about 10% of HN can decompose in a melted layer at the temperatures 200–250 °C. In the case of developed HN dissociation in the melted layer one may expect a formation of bubbles filled with the reaction products.

Recorded in the present study the extended preheat zone (at least a few hundreds of microns) implies acceptable accuracy of measuring the temperature profile in the condensed phase even with 50 μm thermocouples. Important issue is that the thinner thermocouple (10 μm in diameter) recorded the same value of the burning surface temperature. An example of the thin thermocouple readings is shown in Fig. 3. It is seen that the thermocouple signal contains oscillations at the temperatures in the condensed phase higher than the melting point of HN (71 °C).

When analyzing these data, one can find that the temperature profile in the gas phase is very steep with the magnitude of gradient in the zone just above the burning surface being equal to 20–30 K/ μm . In this case an estimated value of the heat feedback from the gas phase is about 50 cal/ cm^2s that provides energetic expenses not only for heating the condensed substance from initial to the burning surface temperature but also for covering essential part of heat loss on evaporation of melted HN (its latent evaporation heat equals 400 cal/g [3]). Acceptable quality of our temperature profile measurements can be proved by the data on the temperature profiles recorded in experiments on combustion of model solid propellants with HN totally replaced by AP. In this case the 50 μm W/Re thermocouple recorded typical steep temperature profile with the value of the burning surface temperature equal to ~ 420 °C.

Additional information about the combustion mechanism and the burning rate behavior can be obtained via analyzing the visualization data and the recoil force records at atmospheric pressure. It looks surprising that despite the relatively low burning surface temperature some of Al particles are ignited close to the surface. The video frames and single shots clearly demonstrate that the Al particles merge and agglomerate on the burn-

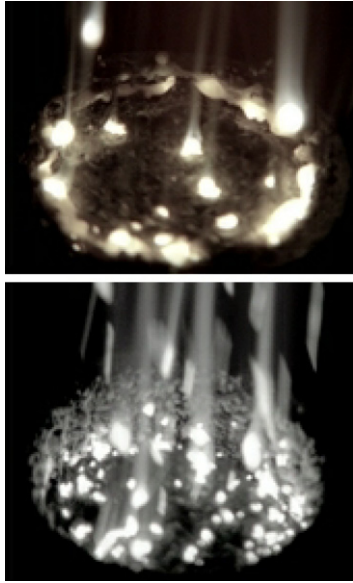


Fig. 4. View of the burning surface of P_1 (top) and P_2 (bottom) propellants, $P = 1$ atm.

ing surface and their residence time on the propellant surface is relatively long. One may expect that the reactions of Al with the products of HN and energetic binder decomposition accompanied by the heating of protruding from the surface agglomerates with the hot gas flame will result in ignition of agglomerates, which then detach from the burning surface. This is what we really observed in experiments on combustion of metallized the HN based propellant samples at atmospheric pressure. Visualization data showed (Fig. 4) that the agglomerates sizes were relatively large and the agglomerates concentration on the burning surface was relatively small in the case of propellant P_1 loaded with commercial Al (5 μm mean particle size). In the case of propellant P_2 (half of commercial Al is replaced by Alex) the agglomerate sizes were smaller and the agglomerates concentration was higher. Roughly, the maximum agglomerate sizes were 300–500 μm in combustion of P_1 and 100–200 μm in combustion of P_2 propellants, correspondingly. These observations turned out in a good agreement with the data of recoil force measurements: larger amplitude and lower frequency of the recoil signal oscillations were observed for the propellant P_1 .

It has to be noted that the relatively large size of agglomerates on the burning surface cannot be explained via analysis of geometrical structure of solid propellants under study. Important point is that the oxidizer grains, used in formulations, had the size less than 63 μm . Therefore, the formation of agglomerates of several hundred microns size is probably the result of non-uniform spatial distribution of metal within the HN/energetic binder matrix and of merging smaller aggregates of metal particles.

The effect of Alex addition on the propellant combustion behavior is similar to that one, which was expected from the previous studies. Indeed, partial substitution (50%) of commercial Al by Alex resulted in shortening the ignition delay and increasing the burning rate magnitude. It is interesting to note

that the pressure exponent in the burning law became higher when replacing partially the commercial Al with Alex. Similar trends were observed in the combustion of AP based propellants [2]. Assuming that the gas phase chemistry is not affected by replacement of Al with Alex, one has to analyze different ways for larger enhancement of the contribution of Alex generated heat release into the heat balance on the burning surface under elevated rather than under relatively low pressures. Consequently, it can be caused by an increased heat release in the condensed phase (higher metal consumption within the condensed phase reaction zone) or by increased heat feedback from the gas phase (more effective ignition and combustion of individual metal particles) at elevated pressures. Due to the lack of comprehensive combustion models the real cause can be determined only in experiments.

Most significant effect on the combustion characteristics of HN based propellants has been observed when changing formulation by replacing an “inert” binder with energetic one. As was mentioned above, the HN/inert binder propellants do not burn in the pressure range 1–100 atm. The HN/energetic binder propellants are shown to readily burn under these pressures. The burning rate of the abovementioned propellants is essentially higher as compared with that for HN/HTPB propellants. For example, at pressure 80 atm the energetic binder based propellant, which contains 9% of commercial Al and 9% of Alex, burns with the rate of 26 mm/s while the HTPB based propellant with the same content of commercial Al and Alex burns with the rate of about 6–7 mm/s.

5. Conclusions

The estimations made in this work testify to reasonably high energetic characteristics of the propellants containing HN, Al, and energetic binder. The theoretical specific impulse of such propellants exceeds that value for AP based propellants of similar formulation by approximately 10 s. The HN based propellants with energetic binder exhibit relatively high burning rate and acceptable pressure exponent ($n = 0.34$ at $P = 40$ –80 atm). Substitution of half of commercial Al by Alex leads to ~ 2 -fold increase in the burning rate and increase in the pressure exponent ($n = 0.57$ at $P = 40$ –80 atm).

Combustion of Al is accompanied by a relatively intense agglomeration resulted in formation on the burning surface of several hundred microns size agglomerates ($P = 1$ atm). Addition of Alex on expense of commercial Al into the propellant formulation decreases the agglomerate sizes, facilitates the ignition of the propellant, and makes wider the flammability pressure range. The completeness of Al combustion in HN based propellants has to be studied in specially designed experiments.

Thermocouple measurements showed surprisingly low burning surface temperature. These measurements must be continued for obtaining most reliable data, which have to be combined with the data on HN evaporation at elevated temperatures and on detailed visual examinations of the burning surface behavior.

References

- [1] V.V. Alexandrov, A.V. Boldyreva, et al., Combustion of DINA under atmospheric pressure, *Fizika Goreniya i Vzryva* (Combustion, Explosion, and Shock Waves) 9 (1) (1973) 140–142.
- [2] A. Dokhan, D.T. Bui, E.W. Price, et al., A detailed comparison of the burn rates and oxide products of ultra-fine Al in AP based solid propellants, in: 34 Annual Conf. of ICT, Karlsruhe, Germany, 2003, Report P 28, 14 pp.
- [3] Yu.I. Rubtsov, G.B. Manelis, Kinetics of thermal decomposition of hydrazinium nitrate, *J. Phys. Chem.* 44 (2) (1970) 396–400 (Russian).
- [4] S.F. Sarnar, *Propellant Chemistry*, Reinhold Publishing Corporation, New York, 1966.
- [5] V.P. Sinditskii, V.V. Serushkin, et al., Flame structure of hydrazinium nitroformate, in: Proc. 5th Int. Symp., Special Topics in Chemical Propulsion, Stresa, Italy, 2000, pp. 576–586.
- [6] V.E. Zarko, G.I. Anisiforov, et al., Study of the combustion of hydrazinium nitrate based model propellants, in: 35th Int. Annual Conf. of ICT, Karlsruhe, Germany, 2004, Report P 91, 14 pp.
- [7] A.A. Zenin, HMX and RDX: combustion mechanism and influence on modern double-base propellant combustion, *J. Propulsion Power* 11 (4) (1995) 752–758.
- [8] A.F. Zhevlakov, V.A. Strunin, et al., Mechanism of combustion of hydrazinium nitrate and the effect of alkaline metal additives, *Fizika Goreniya i Vzryva* (Combustion, Explosion, and Shock Waves) 12 (2) (1976) 185–191.