Defence Science Journal, Vol 48, No 2, April 1998, pp. 211-217

Effect of Burning Rate Modifiers on Subatmospheric Flame Temperatures of AP/HTPB Composite Solid Propellants

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ABSTRACT

Using 30 µm *Pt* and *Pt* 13 per cent Rh thermocouples, flame temperatures of uncatalysed and catalysed ammonium perchlorate/hydroxyl-terminated polybutadiene (AP/HTPB) composite solid propellants were measured under subatmospheric conditions. Ferric oxide Fe_2O_3 and copper chromite (CC) were the catalysts used. The study demonstrates that Fe_2O_3 catalysed propellant, notwithstanding its least combustion efficiency under subatmospheric conditions and weak gas-phase flame, has the maximum burning rate enhancement. This is argued to be due to the increased surface and subsurface reactions caused by Fe_2O_3. CC-catalysed propellant burns to the least subatmospheric pressure with minimum loss in combustion efficiency indicating that this class of propellant may be more suitable for base-bleed applications.

1. INTRODUCTION

Better understanding of subatmospheric and low pressure combustion of solid propellants is necessary for the development of missile base-bleed (BB) propellant grains[1-4] and stop-start solid motors, as well as for accurate prediction of early stages of motor ignition transients. Furthermore, by its (i) gas phase reaction zone consisting mainly of premixed flame[5] (as against competing premixed and diffusion flames at rocket operating pressures), (ii) less severe temperature gradient at the burning surface, and (iii) better spatial and temporal resolutions, the subatmospheric combustion of composite solid propellants offers, for mechanistic study, a simpler perspective of the complex phenomenon. In missile BB applications, the fuel-rich solid propellant grains are required to burn efficiently at subatmospheric pressures[1,3].

Though composite solid propellants, compared to double-base (DB) propellants, burn more efficiently at low pressures, the combustion efficiency falls drastically below certain subatmospheric pressures culminating in extinction. The pressure at which this extinction occurs is termed as low pressure deflagration limit (LPDL), as against the high pressure deflagration limit (HPDL) demonstrated in certain propellants[6].

While the beginning of extensive fuming in burning under subatmospheric pressure[6-8] is a qualitative indication of this reduced combustion efficiency, the reduction in the flame temperature should be a quantitative pointer. The aim of the present study is to investigate the effect of burning rate modifier (BRM) on the flame temperatures of the unmetallised ammonium perchlorate

Received 02 June 1997, revised 24 November 1997

hydroxyl-terminated polybutadiene (AP/HTPB) composite solid propellants, under subatmospheric conditions. The temperatures were measured by using fine thermocouples. The two BRMs used were copper chromite (CC) and Fe_2O_3. Thus, three types of propellant samples were studied: uncatalysed, CC catalysed, and Fe_2O_3 catalysed. The study demonstrated that Fe_2O_3 catalysed propellant, notwithstanding its least combustion efficiency under subatmospheric conditions and weak gas-phase flame, has the maximum burning rate enhancement—possibly due to the increased surface and subsurface reactions. CC-catalysed propellant burns to the least subatmospheric pressure with minimum loss in combustion efficiency.

2. EXPERIMENTAL PROCEDURE

Pt and *Pt* 13 per cent *Rh* thermocouple wires of 99.9 per cent purity and of 30 μm diameter were welded using an *Ar* arc welding apparatus. The two wires were twisted to a length of about 5 mm and held in the apparatus on a movable jaw. The twisted end was inserted into a quartz housing through a small hole on its one end. The quartz housing had a fixed *W* electrode at its other end. The twisted end was adjusted to a gap of about 2 mm from the tip of electrode. *Ar* was passed through the housing at the rate of 10 ml/min and the thermocouple junction was formed by striking an arc through a DC voltage. After a number of trials, 80V DC and 2 mm gap were found to give acceptable bead diameters of values less than twice the wire diameter. The bead diameters were measured using a projection microscope. The thermocouple was calibrated up to a temperature of 1350 °C using the furnace of a differential thermal analyser DTA (DuPont, USA). The standard thermocouple in the furnace had been checked for its accuracy against the melting point of pure *Ag*.

Propellant samples with or without BRM of the mass composition AP: HTPB: 2-ethyl hexyl adipate: toluene diisocynate = 73.00:21.60: 4.05:1.35 were prepared. AP particle size of weight mean diameter ($\Sigma n_i d_i^4/\Sigma n_i d_i^3$), 98.5 μm was used in all propellant samples. Regarding the effect of BRM concentration variation in AP/HTPB and AP/CTPB (carboxyl-terminated polybutadiene) propellants, our earlier studies[6,8] indicated that within the 2 per cent mass concentration of BRM (CC or Fe_2O_3), the burning rate enhancement did not peak up. However, the burning rate enhancement kept on increasing monotonically and started to level off around 2 per cent concentration. On the other hand, 2 per cent mass concentration can generally be taken as the maximum practical limit in a propellant. Therefore, in the present study, 2 per cent mass concentration levels have been chosen for both the modifiers, as these levels correspond to their respective maximum burning rate enhancements.

The propellant was vacuum cast in a rectangular block of 190 x 120 x 40 mm. The thermocouples were inserted at an angle of about 30° to the plane of the uncured propellant surface and the angle between the two thermocouple leads at the insertion point was always seen to be as obtuse as possible. The propellant block, along with the inserted thermocouples, was again kept in the vacuum casting chamber for about 45 min to remove any air entrapped in the propellant during the insertions. The block was then cured in an oven at 80 °C for four days. Propellant strands of 40 x 40 x 100 mm with inserted thermocouples were cut from the above cured propellant block. For burning rate measurements (using fuse-wire cutting technique), propellant strands of 6 x 6 x 180 mm without thermocouples were separately prepared following similar procedures. To ensure uniform burning, the propellant strands were inhibited at their sides with a solution of 10 per cent polyvinyl alcohol.

The experimental setup used for burning rate as well as temperature measurement consisted of a large surge tank and a bell jar connected to a vacuum pump (Fig.1). All-propellant burnings were carried out under *N* atmosphere and in each case, the pressure was held constant by

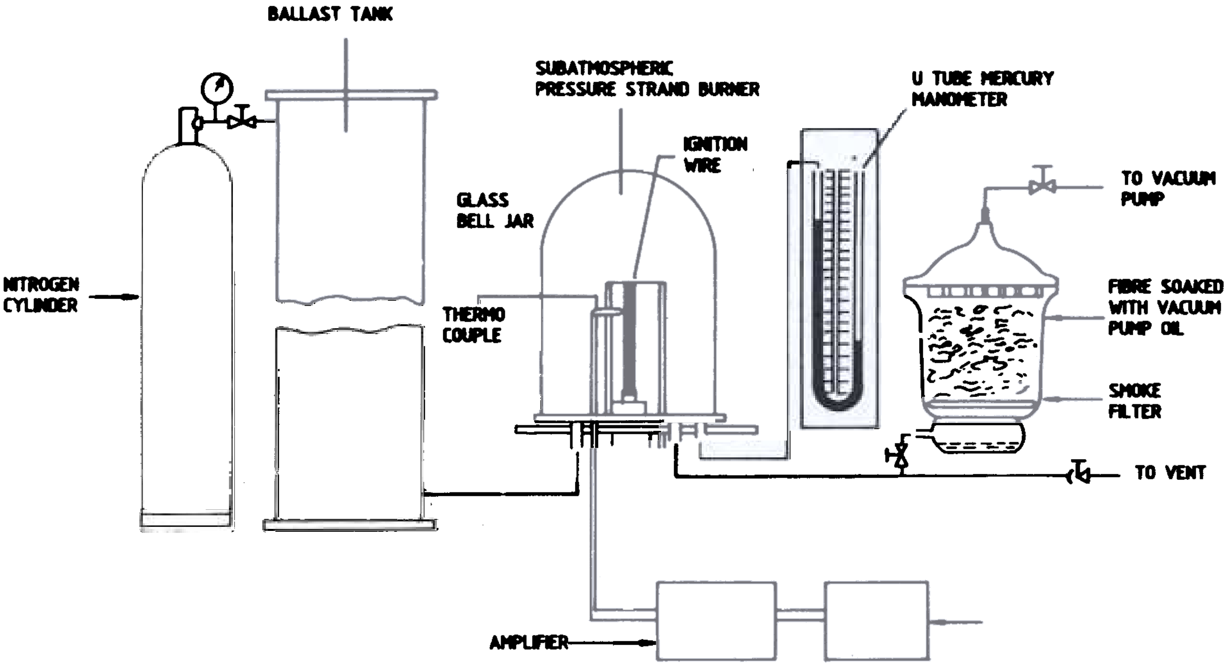

Figure 1. Circuit diagram of te

continuously evacuating the bell jar. Ignition was achieved using a nichrome wire. In the temperature measurement, as the flame-front of the burning propellant approaches and crosses the thermocouple, the corresponding millivolt signals generated were amplified and continuously recorded on a PC/AT at a sampling rate of 200 samples/s. The recorded millivolts *vs* time signals were converted into temperature-time and temperature-distance records employing the calibrated temperature-millivolt curve and the measured burning rate. Flame temperature of the propellant at a particular pressure was taken as the highest temperature in the temperature-time record.

3. RESULTS & DISCUSSION

While burning under subatmospheric conditions, a wide variety of flames were visually observed for the propellant samples. Around 1 bar, all the propellants burn with a blackish smoke and the flame is generally made up of two zones: (i) a base flame of about 1 mm thickness sitting on the surface (light-blue with intense blue boundary near

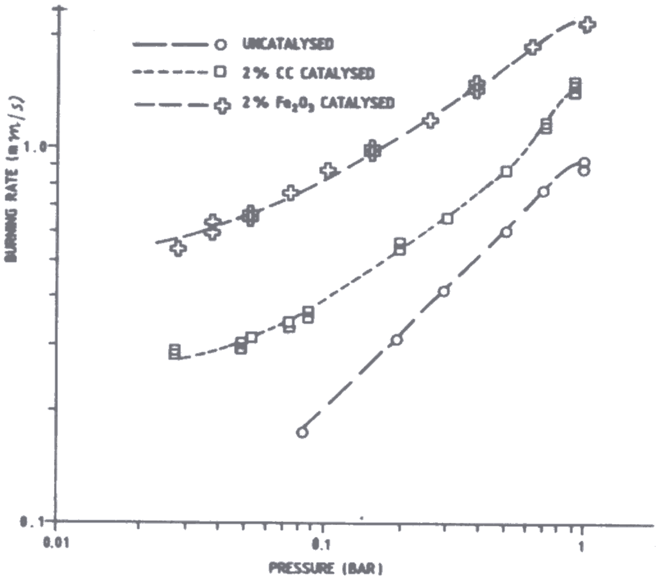

Figure 2. Subatmospheric burning rate characteristics of AP/HTPB propellants.

propellant were observed to be uniform and smooth with less fluctuations—this was clearly discernible near LPDL. The burning rates of the propellant samples are shown in Fig. 2. The maximum burning rate enhancement occurs in the case of Fe_2O_3 catalysed propellant.

Temperature traces of all the propellant samples at various subatmospheric pressures were obtained. Typical ones of 2 per cent Fe_2O_3 catalysed propellant at different pressures are shown in Fig. 3. Every trace shows a smooth rise in temperature till the burning surface of the propellant arrives at the thermocouple junction. This smooth rise in temperature represents temperature variation when the thermocouple junction is within the solid propellant. Thereafter, that is, when the thermocouple junction enters the gas-phase reaction zone, the temperature trace exhibits a steep gradient to enter into the spatially as well as temporally dependent flame temperature fluctuations. These fluctuations are evidently caused by the burning of heterogeneous surface structure of the composite solid propellant. The flame temperature is found to decrease with decrease in pressure indicating the onset of combustion inefficiency.

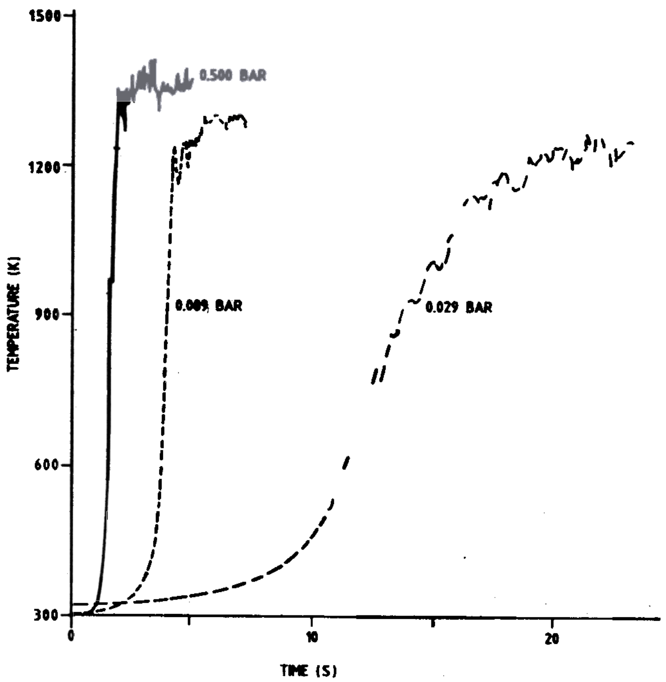

Figure 3. Typical temperature traces of Fe_2O_3 catalysed AP/HTPB propellants.

As the pressure is reduced, the overall (condensed-phase and gas-phase) thermal wave thickness increased with reduced temperature gradient as expected. The thermal wave thickness values were obtained from the temperature traces of all propellant samples at various pressures. The repeatability of these values for a propellant at a chosen pressure was not satisfactory, but for Fe_2O_3 catalysed propellants, the thickness values at various pressures qualitatively appeared to be the largest. Also, as expected, these thickness values for all propellants increased with decrease in pressure.

Typical temperature traces of uncatalysed, 2 per cent CC, and 2 per cent Fe_2O_3 catalysed propellants at 0.3 bar are shown in Fig. 4. The flame temperature of Fe_2O_3 catalysed propellant is significantly lower than those of the other two propellants. Due to strong

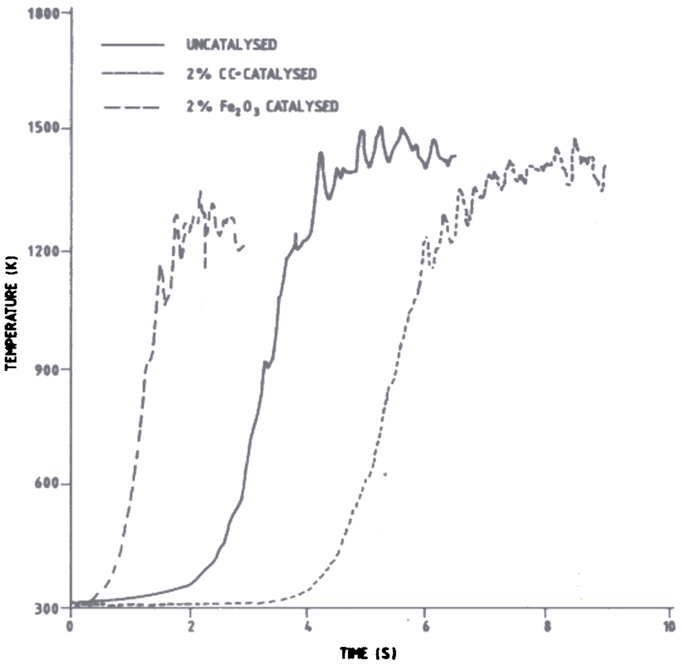

Figure 4. Flame temperature traces of AP/HTPB propellants at 0.30 bar.

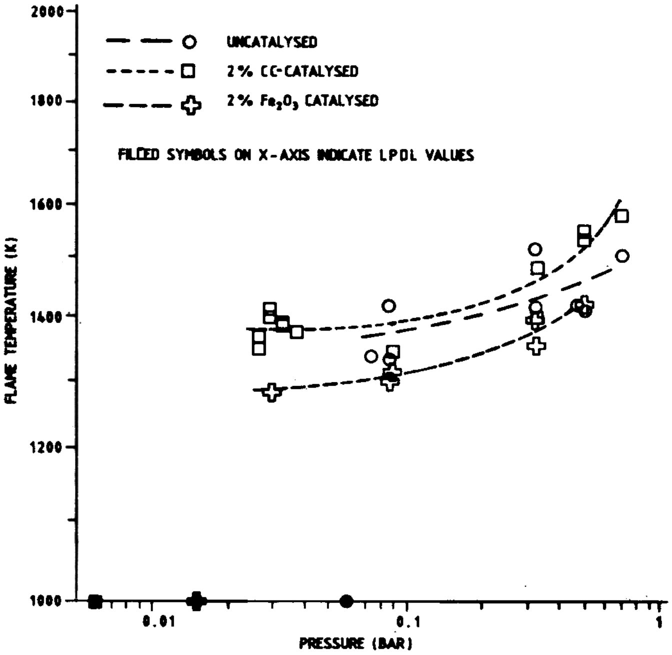

Figure 5. Flame temperatures of AP/HTPB propellants.

flame-fluctuations in uncatalysed propellants, as indicated earlier, their flame temperature values are less repeatable. This is reflected in the combined flame temperature traces for various pressures, (Fig. 5). From this trace, it is seen that the flame temperature decreases with decrease in pressure, the least being that of Fe_2O_3 catalysed propellant. Flame temperatures of uncatalysed and CC-catalysed propellants are not significantly different.

LPDL values of all the three propellants studied are also presented in Fig. 5. It is known that the addition of a catalyst to propellant decreases the LPDL[6-8] and this is also borne out by the present study — CC-catalysed propellant has the least LPDL. Near LPDL, some ejection of partially reacted AP particles occurred, but not to the extent observed earlier for larger AP particle propellants[6,7]

From the above results for subatmospheric pressures, two observations for Fe_2O_3 catalysed propellant need special attention. First, this propellant has a weak and less efficient gas-phase flame, demonstrated by (i) the flame's fading and final-vanishing with reduction in pressure, and (ii) the least flame temperature. Secondly, it has the maximum burning rate enhancement. Addition of a catalyst enhances the regression rate by affecting the reaction rates. The extent to which these rates are affected (in surface and subsurface, and gas-phase regions) may vary among catalysts. Nevertheless, it is not expected to alter the flame temperature at moderate and high pressures[9]. At very low pressures (< 0.1 bar), however, gas-phase combustion is expected to be inefficient, while the surface and subsurface reactions have favourable conditions due to deeper high-temperature penetration into the solid, and thicker and slower thermal wave. The present study shows that Fe_2O_3 propellant has a vanishing gas-phase flame. Also, for this propellant, the flame temperature is measured to be significantly lower than the essentially equal flame temperatures of uncatalysed and CC-catalysed propellants. The burning rate enhancement being maximum for Fe_2O_3 propellant, notwithstanding its weak gas-phase flame, indicated the highest surface and subsurface reactions due to Fe_2O_3. This was further supported by the larger thermal wave thickness. It is believed that with the weak gas-phase flame, a major part of this thickness is due to surface and subsurface reactions. With our present thermocouple diameter of 30 µm, used in present study, it is difficult to estimate accurately the reacting subsurface thickness.

Under subatmospheric conditions, CC-catalysed propellant demonstrates the most stable burning with the least LPDL and without much reduction in flame temperature. This indicates that CC-catalysed propellant is more suitable for BB applications. However, detailed study on the ageing characteristics of this propellant is needed to support this suitability.

4. CONCLUSIONS

Under subatmospheric conditions, the burning rate enhancement for Fe_2O_3 catalysed AP/HTPB propellants is maximum. This is argued to be due to increased surface and subsurface reactions caused by Fe_2O_3. CC-catalysed propellants burn to the least subatmospheric pressure with minimum loss in combustion efficiency, thus making them more suitable for BB applications.

5. ACKNOWLEDGEMENT

The present study forms a part of the research sponsored by the Department of Space, Government of India, through ISRO-IIT(M) Space Technology Cell. SHAR Centre (Sriharikota) of Indian Space Research Organisation supplied the HTPB, di-2-ethylhexyl adipate (DOA), and toluene di-isocyanate (TDI) for the study.

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