Defence Science Journal, Vol 46, No 5, November 1996, pp. 327-330

Effect of Agglomeration on Combustion of Metallized Propellants for Air-Breathing Propulsion System

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ABSTRACT

Combustion phenomena of metallized propellants containing the metals viz. *Mg*, *Zr*, *Al* and *B* with $NaNO_3$ as oxidizer have been studied in order to find out burning rate variations at different oxidizer levels and at different particle sizes of the ingredients. It is found that the burning rate of Mg-$NaNO_3$ and Zr-$NaNO_3$ compositions with finer size $NaNO_3$ shows higher values at lower oxidizer content and decreases with increasing concentration of the oxidizer. In contrast Al-$NaNO_3$ and B-$NaNO_3$ formulations show continuous increase in burning rate with the increase in oxidizer content. Further, the burning rate of all the formulations with $NaNO_3$ of coarser size is found to increase on increasing the oxidizer content. Thermal decomposition results indicate that in the case of *Mg* and *Zr* formulations, decomposition products of finer size $NaNO_3$ formed before reacting to ignition temperature of the metal, react with the metal particles leading to condensed phase heat release causing higher burning rate. An increase of oxidizer content leads to a thicker oxide coating on the metal particles resulting in the formation of metal agglomerates which burn inefficiently in the vapour phase causing lower burning rate. With coarser size $NaNO_3$, due to its decomposition occurring beyond the ignition temperature of the metal particles, reactions shift to the vapour phase diffusion zone causing increase in the burning rate as the concentration of $NaNO_3$ increases. Combustion of *Al* and *B* particles with $NaNO_3$ occurs beyond the melting/ignition temperature of the metal at all the concentrations and particle sizes of oxidizer, causing increase of burning rate with increasing oxidizer content.

1. INTRODUCTION

In recent years, the air-breathing propulsion system has acquired a great importance for use in futuristic medium range missiles[1,2]. Metallized fuels are superior to hydrocarbon fuels as fuel candidates for this system, due to their high heat of combustion and high burning rate[3-5]. However, the use of metallized propellants presents severe problems of complex burning phenomena which have major effects on the energy generation process within the combustor. This is mainly due to agglomeration of the metal particles at the burning surface prior to their ejection into the gas stream depending on the nature of the metal used and the properties of its oxide[6,7]. The problems created by excessive agglomeration include inefficient combustion, effect on the nozzle and expulsion efficiency, variation in the burning rate and a reduction in the flame temperature and specific impulse. This paper presents an extensive study carried out on the metallized propellants containing the metals *Mg*, *Zr*, *Al* and *B* with $NaNO_3$ as an oxidizer in order to find out variations in burning rate properties at different oxidizer levels and particle sizes of the ingredients.

2. EXPERIMENTAL DETAILS

Propellant formulations containing sodium nitrate of particle sizes of 50 μ and 250 μ with metal powders of magnesium (50 μ), aluminium (50 μ), zirconium (10-15 μ) and boron (1-2 μ), at different mixture ratios have been studied. To evaluate burning rate, the propellant grains of 100 mm diameter and 50 mm length were pressure moulded to a density of 1.6 g/cc and inhibited with epoxy resin.

Received 02 September 1996

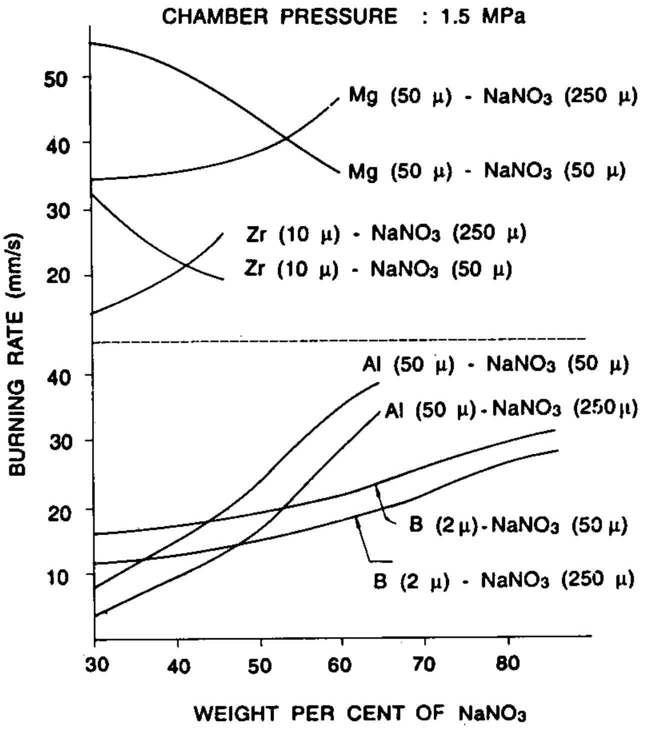

Figure 1. Burning rate of propellants as a function of $NaNO_3$ concentration.

The burning rate of the propellant was determined by static evaluation of the propellant in a test motor. The propellant was ignited electrically with a Mg/KNO_3 based igniter composition. The burning rate was determined from the pressure-time profile.

The DTA of the samples was carried out by using STA 409 NETZSCH, DTA apparatus under atmospheric conditions.

3. RESULTS & DISCUSSION

Burning rates of the propellants containing different weight per cent and particle sizes of $NaNO_3$ are shown in Fig. 1. It can be observed that the burning rate of Mg-$NaNO_3$ and Zr-$NaNO_3$ propellants in the presence of finer size $NaNO_3$ is higher at lower oxidizer content and decreases with increasing concentration of the oxidizer. In contrast, Al-$NaNO_3$ and B-$NaNO_3$ propellants show continuous increased burning rate with the increase in oxidizer content. The burning rate of all the formulations with coarser $NaNO_3$ was found to increase on increase in the oxidizer content. Further, it is found that the burning rate of the propellants increases with decreasing particle size of metal particles due to the faster rate of heat transfer with the increase in surface area of the particles.

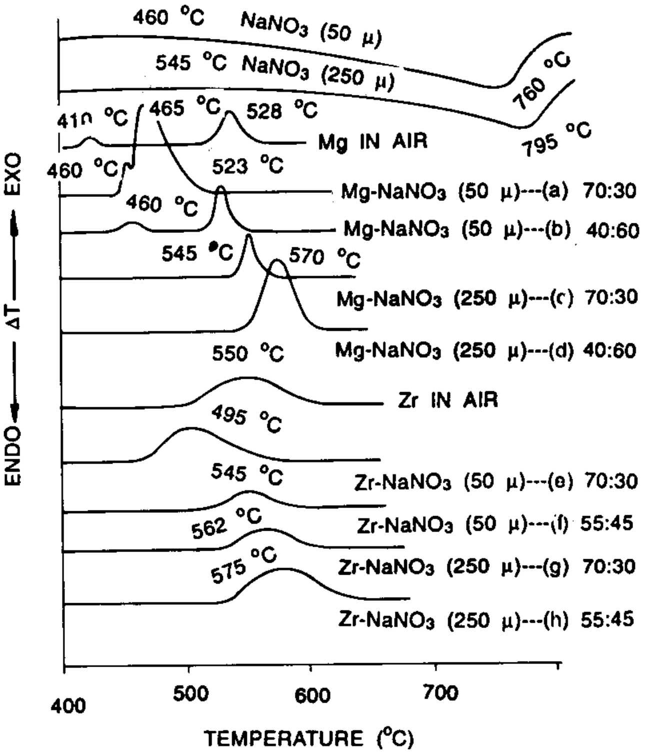

Figure 2. DTA data of *Mg* and *Zr* particles and metal-$NaNO_3$ propellants.

Thermal decomposition studies were conducted to understand the combustion mechanism of these propellants. The results for Mg-$NaNO_3$ and Zr-$NaNO_3$ are shown in Fig. 2 and those for Al-$NaNO_3$ and B-$NaNO_3$ are shown in Fig. 3. The endothermic decomposition of finer size $NaNO_3$ starts at 460 °C and completes at 760°C (Fig. 2). *Mg* particles heated in air showed two exotherms at 410 °C and 528 °C respectively. The first exotherm indicates self heating and the second exotherm corresponds to total ignition of the *Mg* particles.

Thermal decomposition of $Mg/NaNO_3$ propellant (Fig. 2, curve a) indicates two exotherms. The first exotherm appears at 460 °C and the second exotherm at 465 °C with fuel rich composition ($Mg/NaNO_3$=70:30). Further, it is seen that with the increased oxidizer concentration (Fig. 2, curve b), the heat evolution in the exotherm reduces with a subsequent delay in the total ignition.

The exotherm at 460 °C in the DTA indicates that there is a significant interplay between the oxidizer decomposition products and the self-heated *Mg* particles before the particles attain the ignition temperature (528 °C) leading to condensed phase heat release. The large release of condensed phase heat, explains the high burning rate of the propellant at low oxidizer content. Higher concentration of *NaNO3* increases the inert heating of the metal particles due to the higher concentration of the molten oxidizer resulting in a thicker oxide coating on the metal particles. This reduces the heat release in the condensed phase and leads to higher ignition temperature, as observed from DTA. The delay in ignition, results in the formation of metal agglomerates which when ejected into the flame zone, burn inefficiently and result in low burning rate of the propellant.

Thermal decomposition of *Zr-NaNO3* propellant (Fig. 2, curve b) at fuel rich ratio indicates a broad exotherm in the range of 472 °C to 495 °C accounting for high heat evolution for a longer duration. At stoichiometric ratio (55:45) (Fig. 2, curve f), there is a shift in the decomposition range with a reduction in the heat release of the sample. The decomposition of the propellant at high fuel content, occurring before the ignition temperature of *Zr* particles (550 °C), indicates that the formation of oxide envelope around the metal particles (being soluble oxide with the metal) allows the diffusion of the oxidizer species to reach the metal surface for the surface reactions. The release of higher surface heat energy accounts for higher burning rate of the propellant at fuel rich ratio.

At stoichiometric ratio of the propellant in the presence of higher concentration of molten oxidizer, the metal particles are expected to be largely covered with oxide, which reduces the surface oxidation process and causes the reduced exotherm in DTA with a delay in ignition. The ejection of the oxide-covered particles to the vapour phase and their inefficient burning lead to the reduced burning rate. Thus *Mg-NaNO3* and *Zr-NaNO3* propellants with fine particle size *NaNO3* burn in a dual fashion into surface and vapour phase, depending on the fuel-oxidizer ratio and particle size of *NaNO3*.

The decomposition of coarser particle size *NaNO3* which starts at 545 °C is a fast process with a maximum occuring at 795 °C, after the ignition of metal particles (Fig. 2). This causes the absence of condensed phase reactions, as seen in the DTA (Fig. 2, curves c,d,g and h) and the presence of an exotherm at higher temperature suggests total ignition of the sample in the vapour phase.

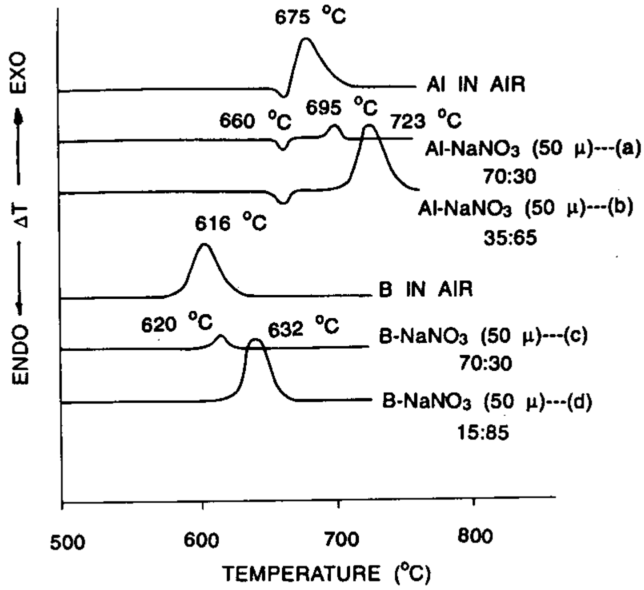

Figure 3. DTA data of *Al* and *B* particles and metal-*NaNO3* propellants.

This combustion then leads to conduction of heat to the burning surface for further regression of the propellant. This explains why the burning rate increases as the proportion of coarser particle size oxidizer increases up to the stoichiometric ratio.

The lower heat release in the vapour phase at high fuel content when the coarser *NaNO3* is present, explains the lower burning rate. In this case, the combustion of metal agglomerates occurs with lower concentration of *NaNO3*. Increasing concentration of the coarser oxidizer, as the mixture ratio approaches stoichiometry, increases both the metal agglomeration due to the high concentration of molten oxidizer and the flame zone temperature, because the combustion of metal agglomerates in the presence of sufficient oxidizer species occurs more efficiently than for stoichiometric compositions with the finer size *NaNO3* (Fig. 2).

The decomposition of *Al-NaNO3* propellant (Fig. 3, curve a) at 695 °C with a lower heat release at fuel rich ratio and at 723 °C with a higher heat release at stoichiometric ratio (Fig. 3, curve b) occurs after *Al* particles attain sufficient energy for melting (660 °C). This delay in ignition is due to the protective oxide layer around the metal particles which thickens further in the presence of molten oxidizer layer, preventing the surface oxidation at lower temperature. The molten *Al* droplets in the absence of the oxidizer species coalesce into large, slow-burning agglomerates at the surface and diffuse out to react in the vapour phase after attaining sufficient surface temperature. This explains the increase of burning rate when the composition approaches from fuel rich to stoichiometric value

Thermal decomposition of *B-NaNO3* propellant (Fig. 3, curves c and d) indicates an exotherm at 620 °C with a lower heat release at fuel rich ratio and at 632 °C, with a higher heat release at stoichiometric ratio. The combustion of the propellant occurring after the boron particles attain the ignition temperature (616 °C) indicates the absence of condensed phase reactions and causes the diffusion of the oxidizer species to the vapour phase. This leads to increase in the burning rate of *B-NaNO3* propellant with increase in the oxidizer content towards stoichiometric ratio.

The increase of particle size of oxidizer with *Al* and *B* based propellants lowers the burning rate of the propellants in comparison~~to the propell~~ants containing finer particle size oxidizer without affecting the burning rate pattern. This is because of the long residence time of the molten layer of the oxidizer at the burning surface before its decomposition, resulting in the increased degree of metal particle agglomeration

ACKNOWLEDGEMENT

The authors are grateful to Dr Haridwar Singh, Director, HEMRL, Pune, for his valuable guidance and encouragement in the preparation of this paper.

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