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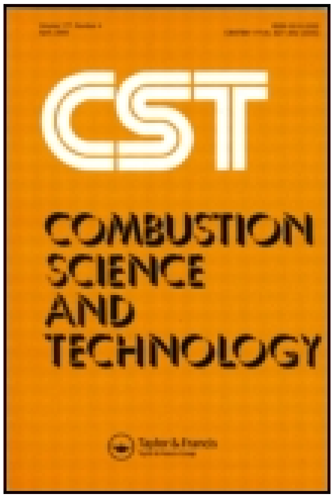

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A Combustion Study of Metal Powders in Contact with Sodium Nitrate

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A Combustion Study of Metal Powders in Contact with Sodium Nitrate

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ABSTRACT—Combustion phenomena of metal powders in contact with $NaNO_3$ used as propellants have been studied in order to find out burning rate variations at different oxidiser levels. Commonly used metals like Mg, Al, Zr and B (a metalloid) have been considered for the present study. It is found that the burning rate of the propellants largely depends on mixture ratio of the fuel and oxidiser. The burning rate of Mg-$NaNO_3$ and Zr-$NaNO_3$ propellants decreases with increasing concentration of $NaNO_3$ in contrast to the energy content of the propellants. On the otherhand the burning rate as well as the energy content of Al-$NaNO_3$ and B-$NaNO_3$ propellants increases with increasing $NaNO_3$ concentration.

Thermal decomposition results indicate that propellants containing Mg and Zr at low oxidiser content have higher condensed phase/surface heat release before the metal particles acquire sufficient energy for ignition and hence provide surface mode of combustion leading to high burning rates. At higher oxidiser contents, they have a lower heat release in the condensed phase and at the surface with a delay in ignition due to the oxide coating of the metal particles in presence of higher concentration of molten oxidiser, thus provide vapour phase combustion leading to low burning rates. In contrast, decomposition of the propellants containing Al and B occurring after the metal particles acquire sufficient energy for ignition due to the presence of protective nature of their oxide layers around the metal particles leading to vapour phase combustion at all mixture ratios. This causes an increase of burning rates with increasing oxidiser content of the mixture upto the stoichiometric ratio. The burning surface temperature data and the photographs of partially burnt samples also support the suggested mechanism.

Key Words: Metal-Oxidiser propellants, effect of $NaNO_3$, burning rate, combustion, thermal decomposition, metal agglomeration

INTRODUCTION

Metal powders are of great interest as fuel ingredients for air-breathing ramjet systems because of their high heat of combustion and high burning rate. Among the various metals, magnesium, aluminium, zirconium and boron (a metalloid) are typical components of high energy fuels (Schadow, 1972; King, 1976; McClendon, *et al.*, 1980) and have received a great attention for fuel rich propellants for use in ducted-rockets. However, the practical use of these fuels present severe problems of complex burning phenomena which have major effects on the energy generation process within the combustor. Since the performance realisation of a propellant depends on its kinetic as well as energetic parameters, the factors affecting the combustion behaviour like propellant formulation, fuel-oxidiser ratio, metal particle agglomeration and other combustion phenomena should be known in detail.

The combustion behaviour of the metals largely depends on the physical properties of the metals and their oxides. Metal particles during burning tend to accumulate on the burning surface and generally form aggregates that coalesce into large slow burning agglomerates causing incomplete combustion and poor combustion efficiency. Because of this property the metal combustion is quite varied than other ingredients of the propellant and the particular effect depends on the metal and nature of the oxidiser used.

Many studies have been devoted in the past on the combustion mechanism of metal particles directly introduced into an oxidising gas but a very limited studies have been carried out (Beardell,. *et al.*, 1972; Northam, *et al.*, 1973; Chen, *et al.*, 1991) on the combustion of metal particles with the various solid oxidisers. In the present work, experiments have been carried out to study the effect of the fuel-oxidiser ratio on the burning rate and energetic performance of the metal loaded propellants using common metals like Mg, Zr, Al and B and fuels. Attempts have also been made to develop a suitable combustion mechanism in order to provide a reasonable description of the results obtained.

EXPERIMENTAL

Propellant formulations containing sodium nitrate (50 μ) with metal powders viz magnesium (50 μ), aluminium (50 μ), zirconium (10–15 μ) and boron (1–2 μ), at different mixture ratios have been studied in the present work. To evaluate burning rate and burning surface temperature, 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.

Burning Rate

The burning rate of the propellant, in end-burning mode, was determined in a test motor of 110 mm diameter by static firing. The ignition end of the grain was prime coated with a Zr/KNO_3 based composition. The propellant was loaded in the test motor and ignited electrically with a Mg/KNO_3 based igniter composition. The burning rate was determined from the pressure time profile.

Heat of Combustion

The heat of combustion values were determined with a Julius Peters adiabatic bomb calorimeter of 300 cc volume. The sample corresponding to 0.01 g/cc loading density was ignited in an argon atmosphere at 15 kg/cm^2 pressure level.

Differential Thermal Analysis (DTA)

The DTA of the samples were measured using STA 409 NETZSCH, DTA apparatus. Samples were operated at atmospheric pressure level. The sample weighing 5–10 mg was used for each test.

Surface Temperature

Surface temperature of the propellants at different metal-oxidiser ratios were measured during the static firing with micro-thermocouples embedded within the sample. Micro-thermocouple made of platinum and platinum-rhodium 10% of 50 μ diameter was used. The method of embedment of thermocouple in the propellant grain was described by Harihar Singh, *et al.* (1992).

Partially Burnt Residue

The propellant grains were ignited in a test motor and the partially burnt residues at different formulations and mixture ratios, left in the motor due to inefficient burning were collected and photographed to 100X magnification with a scanning electron microscope.

RESULTS AND DISCUSSION

Burning rate of the propellants at different weight percent of $NaNO_3$ is shown in Figure 1. It can be observed that the burning rate of Mg–$NaNO_3$ and Zr–$NaNO_3$

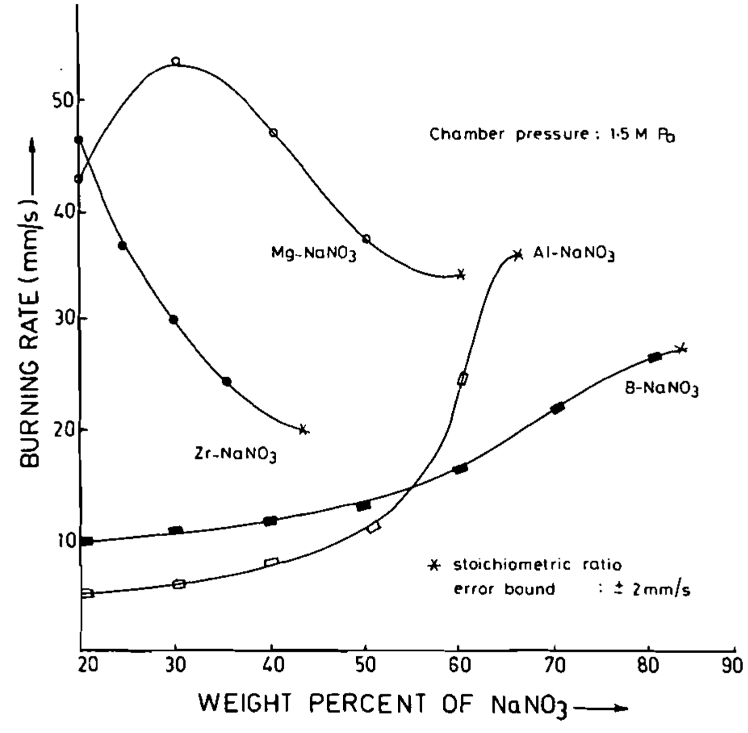

FIGURE 1 Burning rate of propellants as a function of $NaNO_3$ concentration.

propellants is higher at lower oxidiser content (fuel rich) and reaches a lower value at higher oxidiser content of the mixtures (i.e. at stoichiometric point). On the other hand the burning rate of Al–$NaNO_3$ and B–$NaNO_3$ propellants is low at lower oxidiser content and reaches a maximum vlaue at stoichiometric ratio of the mixtures. Further at fuel rich ratio the burning rate of the propellants containing Mg is higher than Zr followed by B and Al. Whereas, at stoichiometric ratio of the mixtures, the burning rate is higher with Al than Mg followed by B and shows a low value with Zr based propellant.

Heat of combustion data of the propellants at different oxidiser concentrations (Fig. 2) show that heat energy gradually increases up to the stoichiometric point of the compositions with all the fuels unlike the burning rate. Further the heat content at fuel rich ratio of the propellant containing Mg is higher than Al followed by Zr and shows a lower value with B. This indicates that the burning behaviour of the propellants is quite different than their energetics. The heat energy of the propellant depends on the fuel-richness of the composition, its combustion products and the gravimetric heating value of the fuel, whereas the burning rate a kinetic parameter, is highly dependent on the physico-chemical properties of the fuel and the oxidiser of the propellant.

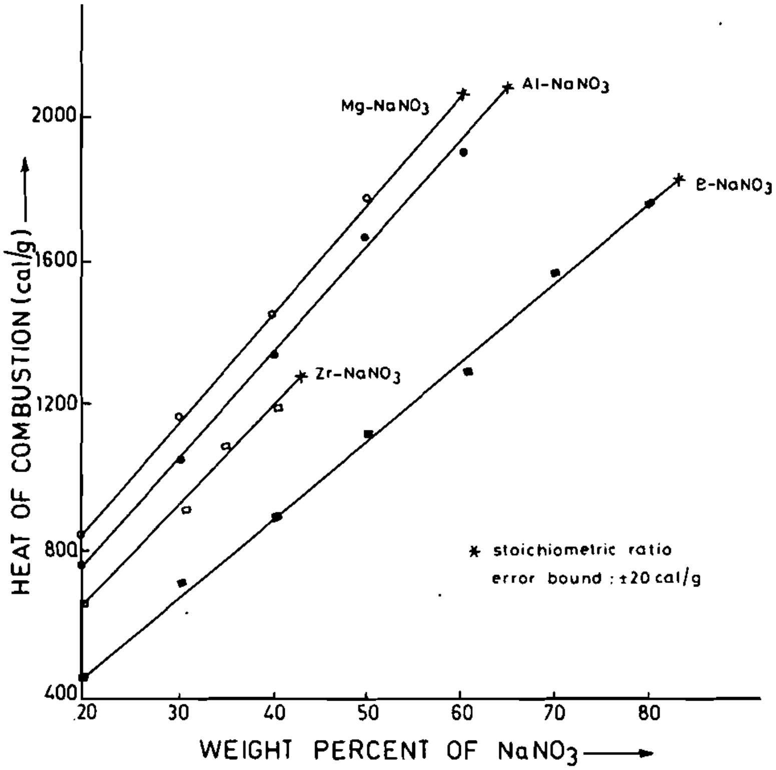

FIGURE 2 Heat of combustion of propellants as a function of $NaNO_3$ concentration.

To obtain the information on the heat content at the burning surface of the propellant, the burning surface temperature was determined. The results indicate (Fig. 3) that with all the propellants the surface temperatures are higher at stoichiometric point of the compositions. Also the surface temperature is higher with the propellant containing Al than B followed by Zr and shows a lower value with Mg.

To understand the combustion mechanism of the propellants, thermal decomposition studies were conducted. Results for $NaNO_3$, Mg and Mg–$NaNO_3$ are shown in Figure 4. The endothermic decomposition of $NaNO_3$ starts at 460°C after a melting transition at 308°C and completes at 760°C. Mg particles heated in air showed two exotherms at 410°C and 528°C. The first exotherm indicates self heating, probably associated with the oxide film becoming non-protective being porous in nature (Mellor and Glassman, 1965) and the second exotherm corresponds to total ignition of the Mg particles.

Thermal decomposition of Mg/$NaNO_3$ propellants indicates two exotherms. The first exotherm appears at 460°C and the second exotherm at 465°C with fuel rich composition and at 523°C with stoichiometric composition. Because $NaNO_3$ starts decomposing at 460°C endothermically, the first exotherm at 460°C with the propellant can be accounted for by the exothermic oxidation of Mg by $NaNO_3$ decomposition products in the condensed phase. The second exotherm corresponds to total ignition of the sample. Further it is seen that with the increased oxidiser concentration (stoichiometric ratio), the heat evolution in the exotherm reduces with a subsequent delay in the total ignition.

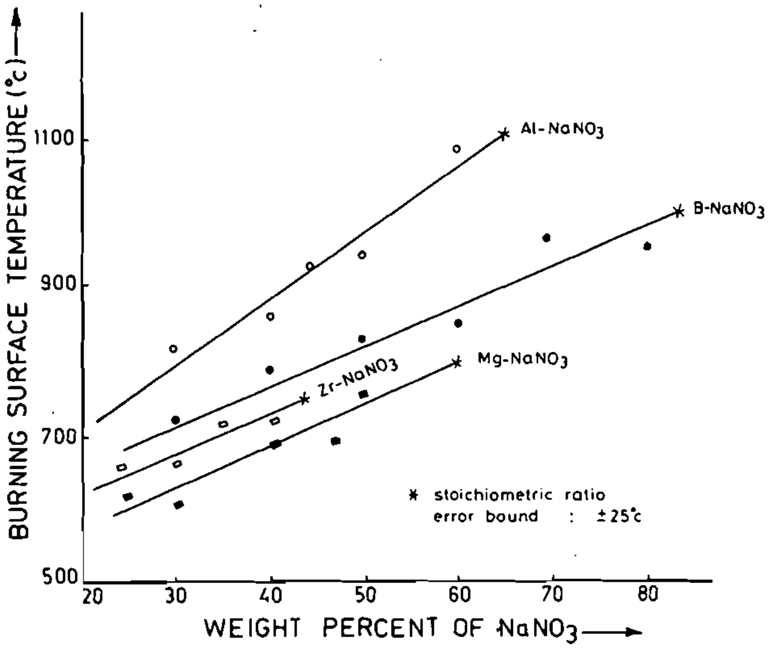

FIGURE 3 Burning surface temperature of propellants as a function of $NaNO_3$ concentration.

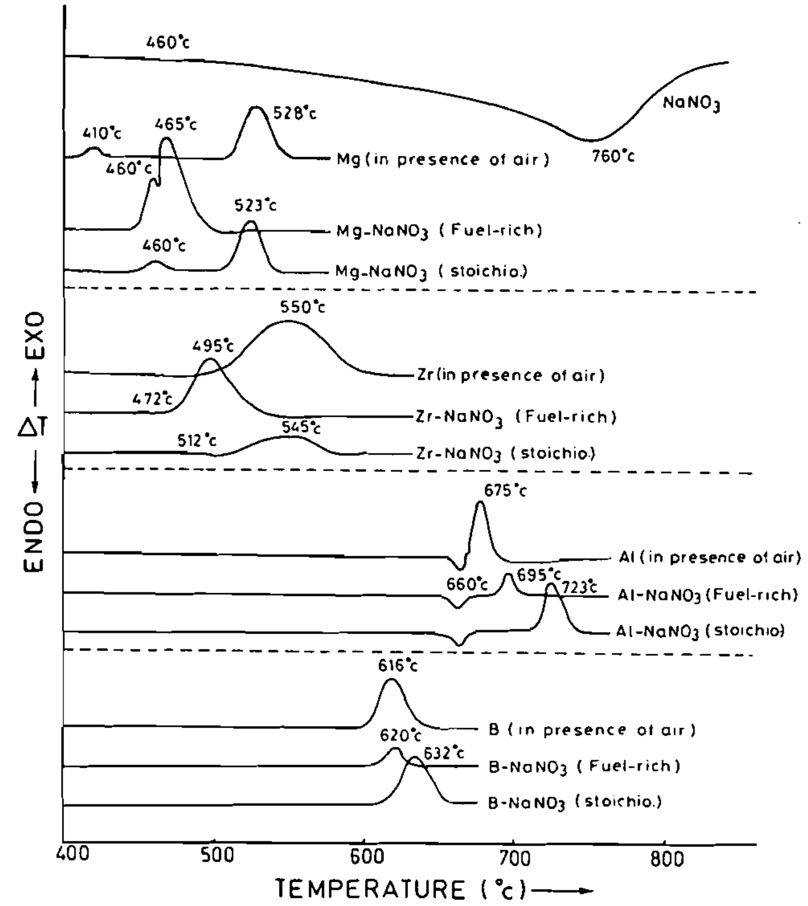

FIGURE 4 DTA data of Mg, Zr, Al and B Particles heated in air and metal-$NaNO_3$ propellants heated in argon.

It has been suggested by Bond *et al.* (1966) that the decomposition of $NaNO_3$ proceeds from nitrate to nitrite with the release of atomic oxygen. This oxygen atom reacts with Mg for the exothermic heat release and facilitates total ignition of the sample. The exotherm at 460°C in the DTA indicates that there is a significant interplay between the oxidiser decomposition products and the shelf heated Mg particles before the particles reaches the ignition temperature (528°C) leading to condensed phase heat release. The large release of condensed phase heat indicated in the DTA at 460°C followed by high exothermic heat release at 465°C (Fig. 4 Mg–$NaNO_3$ fuel rich) explains the high burning rate with Mg–$NaNO_3$ propellant at 30% $NaNO_3$ content.

Higher concentration of $NaNO_3$ increases the inert heating of the metal particles due to the higher concentration of the molten oxidiser 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 that, when ejected into the flame zone burn inefficiently and leave partially burnt samples. The photograph of the samples clearly indicate the state of the surface (Fig. 5a).

Particle agglomeration of magnesium at stoichiometric ratio and the corresponding delay in ignition may cause the diffusion of oxidiser species to the flame zone away from the surface without accompanying magnesium particles. Diffusion of Mg agglomerates take place to the flame zone only after the particles attain a sufficient temperature on the burning surface (R. B. Rao *et al.*, 1995). This may cause rise in burning surface temperature as observed from Figure 3 when the composition approaches stoichiometric ratio.

Thermal decomposition of Zr–$NaNO_3$ propellant at fuel rich ratio indicates a broad exotherm (Fig. 4) in the range of 472°C to 495°C accounting for high heat evaluation for a longer duration. At stoichiometric ratio 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) in a slow process. This indicates that in presence of lower concentration of molten oxidiser around the metal particles the thickness of the oxide envelope is low and it allows the diffusion of the oxidiser species (being soluble oxide with the metal) 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. The surface reactions with Zr owing to the property of the oxide solubility with the metal are in accordance with Gorden (1960).

At stoichiometric ratio of the propellant in presence of higher concentration of molten oxidiser, the metal particles are expected to largely covered with oxide which reduces the surface oxidation process and causes the reduced exotherm in DTA with a delay in ignition (Fig. 4). This may cause the diffusion of oxidiser species to the vapour phase and results in the increased burning surface temperature before the particles acquire sufficient energy for ejection to the vapour phase due to the pressure forces. The ejection of the oxide covered particles to the vapour phase and the inefficient burning leads to the reduced burning rate. Thus Mg–$NaNO_3$ and Zr–$NaNO_3$ propellants burn in a duel surface and vapour phase mode depending on the fuel-oxidiser ratio.

Since the melting point of Zr (1852°C), unlike Mg (650°C), is very high and is much above the burning surface temperature (800°C) of the propellant, the particle agglomeration is expected of very low order (Fig. 5b). The lower burning rate of the propellants containing Zr than Mg are attributed to their difference in the energy content (Fig. 2).

The decomposition of Al–$NaNO_3$ propellants (Fig. 4) at 695°C with a lower heat release at fuel rich ratio and at 723°C with a higher heat release at stoichiometric ratio 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 enhances further in presence of molten oxidiser layer, preventing the surface oxidation at lower temperature. The molten Al droplets in absence of the oxidiser species coalesce into large slow burning agglomerates at the surface as seen from the photograph (Fig. 5c) and diffuse out to react in the vapour phase after attaining sufficient surface temperature. The combustion in the vapour phase conducts heat to the burning surface for further regression of the propellant. This explains the increase of burning rate when the composition approaches from fuel rich to stoichiometric value. The high degree of

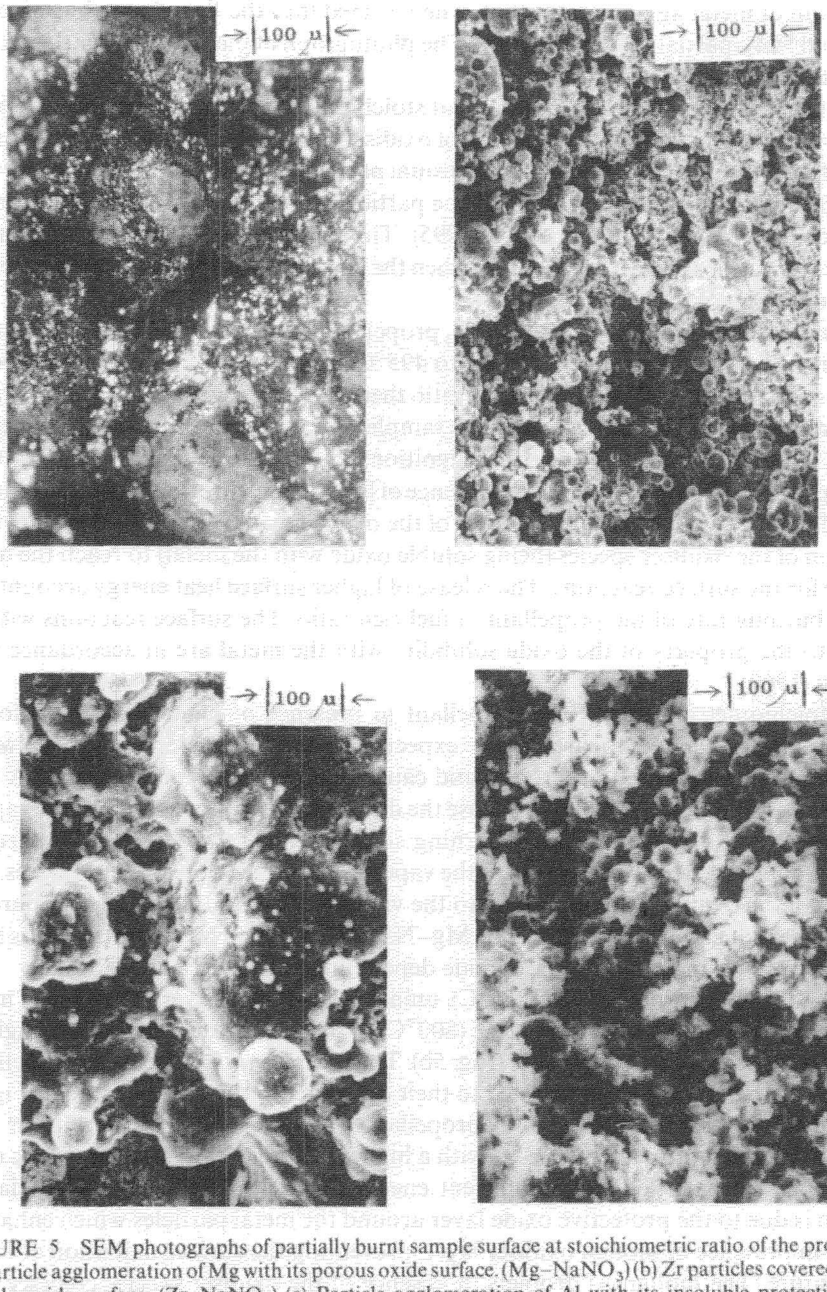

FIGURE 5 SEM photographs of partially burnt sample surface at stoichiometric ratio of the propellants (a) Particle agglomeration of Mg with its porous oxide surface. (Mg–$NaNO_3$) (b) Zr particles covered with its soluble oxide surface. (Zr–$NaNO_3$) (c) Particle agglomeration of Al with its insoluble protective oxide surface. (Al–$NaNO_3$) (d) Boron particles covered with its protective liquid oxide layer. (B–$NaNO_3$).

agglomeration alongwith protective oxide layer at the surface explains the higher surface temperature than the other propellants.

Unlike Al, the melting temperature of boron is too high (2027°C) than the propellant burning surface temperature (1000°C) to melt the B particles at the surface. On the other hand due to the lower melting temperature of its oxide (450°C), the metal particles are expected to cover with liquid oxide layer and hence the burning rate may become limited depending on the heat available to evaporate the oxide from the particle surface. According to Faeth (1984) the oxidation of boron particles requires that the surrounding gas temperature be about 1627°C, which is only possible in the flame zone than at the surface.

Thermal decomposition of B–$NaNO_3$ propellant (Fig. 4) 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. When boron particles heated in air, the exothermic reaction occurred at 616°C. According to Yataka Yano (1989), the oxidation of boron particles starts from the surface of each boron particle and form an oxide shell around the surface. The penetration of the oxidiser species through the oxide shell towards the interior portion of the particle becomes difficult. Hence the combustion of the B/$NaNO_3$ propellant observed in the DTA measurement after the boron particles attaining the ignition temperature (616°C) indicates the absence of condensed phase or surface reactions and the delay in ignition causes the diffusion of the oxidiser species to the vapour phase. This is in agreement with the experimental observation of Gany and Netzer (1986) on the combustion of boron containing fuels by means of high-speed photography. The burning of the particles in the gaseous medium favours the increase of the burning rate of the propellants with the increased oxidiser species. This explains why the burning rate of B–$NaNO_3$ propellant increases with increasing oxidiser content towards stoichiometric ratio. The presence of higher concentration of molten oxidiser at stoichiometric ratio increases the particle agglomeration of boron as seen from the photograph (Fig. 5d) and leads to higher surface temperature (Fig. 3).

The surface temperature variations of the propellants is well in agreement with the nature of the metal oxide and metal agglomeration. Al which forms higher degree of metal agglomerates with a protective oxide layer records the highest surface temperature, whereas, the Mg due to its porous oxide nature alongwith agglomeration indicates lowest surface temperature. The surface temperature of B and Zr propellants with low metal agglomeration but with a thicker oxide film around the metal particles lies in between the surface temperatures of Al and Mg. B with a stable liquid oxide layer around the particles records the higher surface temperature than Zr which allows the diffusion of the oxygen through its oxide layer due to soluble nature of its oxide with the metal.

CONCLUSIONS

The following conclusions are drawn based on the present study.

The burning of metal powders in presence of $NaNO_3$ occurs at the propellant surface and/or in the gaseous medium depending on the nature of the metal and its oxide, fuel-oxidiser ratio and degree of agglomeration.

The combustion of Mg particles with $NaNO_3$ is highly effective at low oxidiser content and provides higher burning rate due to condensed phase heat release. However, increasing oxidiser content reduces the heat release in the condensed phase due to oxide coating of the metal particles with the higher concentration of the molten oxidiser leading to the formation of metal agglomerates which burn inefficiently in the vapour phase causing low burning rate.

Combustion of Zr particles with $NaNO_3$ at low oxidiser content occurs at the surface before the particles acquire energy for ignition and release surface heat energy leading to high burning rate. At higher oxidiser content the formation of high degree of oxide covered layer around the metal particles reduces the surface heat energy and the particles burn inefficiently in the vapour phase leading to low burning rate.

Combustion of Al particles in presence of $NaNO_3$ occurs after the melting of the particles without any surface reactions due to the presence of protective oxide layer (insoluble oxide) around the metal particles. This leads to particle agglomeration and the ejection of the agglomerates to the vapour phase causing increase of burning rate with increasing oxidiser content.

Combustion of B particles with $NaNO_3$ occurs after the particles acquire sufficient energy for ignition since the particles are covered with liquid oxide layer (volatile oxide) having very low melting (450°C) and high boiling point (2250°C). The increase of oxide layer with increasing oxidiser concentration and the particle ejection from the surface leads to vapour phase reactions. Thus the vapour phase reactions can cause an increase in the burning rate with increasing oxidiser content similar to Al particles.

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