

REVIEW PAPER

## Metallised Fuel-rich Propellants for Solid Rocket Ramjet – A Review

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### ABSTRACT

This paper reviews the research work carried out in the field of metallised fuel-rich propellants (FRP). Limitations and merits of various potential metals (*Al*, *Mg*, *B*, *Be*, or *Zr*) as a component of FRP are discussed. The paper also includes a discussion on the combustion mechanism of metallised propellants, including problem areas and probable remedial measures. Zirconium and *Ti* appear to have potential to offer FRP with efficient combustion. Ideal performance is not achieved with current systems based on *Al* and *B* and further work is needed to develop FRP having all three desirable attributes, viz., ease of ignition, stable combustion and high specific impulse ( $I_{sp}$ ) in a single composition.

### 1. INTRODUCTION

Fuel-rich propellants (FRP) with high metal content find use in ram-rocket engines. The latter operate with the combustion of fuel-rich hot gases generated in primary combustor and the ram air inducted from the atmosphere to a secondary combustor for full combustion. When used in this fashion, the propulsion system is known as IRR (integrated rocket ramjet) (Fig. 1). Thus, the major benefit of ram rockets is the substantially reduced missile weight, as the oxidiser need not be carried along with the propellant<sup>1</sup>. Metals are incorporated in propellants primarily to achieve high volumetric energy release due to their high heat of reaction with oxygen, improvement in propellant density, reduction in pressure index ( $n$ ) and suppression of combustion instability<sup>2</sup>. Occasionally, metals are also used in the form of wire, foil and screen to enhance burn rates and reinforce mechanical properties<sup>2</sup>. Aluminium (*Al*), magnesium (*Mg*), boron (*B*), zirconium (*Zr*) and beryllium (*Be*) have found wide application as FRP ingredients. FRP formulations for ram rockets comprise metal fuels, binder and minimum quantity of oxidiser to ensure sustained combustion.

These formulations are prepared by adopting well known techniques of extrusion or casting<sup>3,5</sup>. Compositions containing higher solid loadings (>92 per cent) are generally obtained by mixing various ingredients and pressing them in a suitable form<sup>2,3</sup>. Since most of the literature on FRP is scattered, an attempt has been made in this review paper to broadly cover important features of metallised FRP with emphasis on their combustion behaviour.

### 2. METALS AS PROPELLANT FUEL

Aluminium is a widely used metal in highly filled composite (CP) and composite modified double base (CMDDB) propellants. The optimum level of *Al* in these systems is 20 per cent. Beyond this concentration, increase in mean molecular weight of exhaust products ( $Al_2O_3$ ) results in overall loss in specific impulse ( $I_{sp}$ ). However, FRP with high *Al* content poses combustion efficiency and ignition problems due to typical combustion behaviour<sup>6</sup> of *Al*. Therefore, efforts are on to replace *Al* by other metal components of FRP to eliminate these problems. Although, *Mg* has the drawback of low air/fuel ratio (3.29) for ramjet

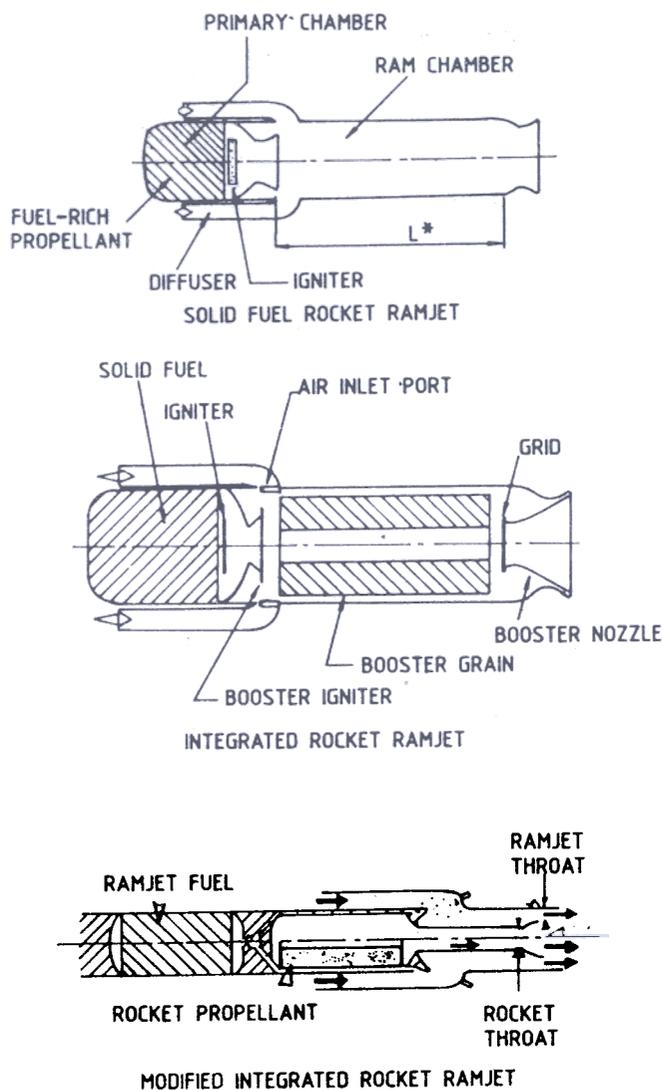


Figure 1. Ramjet variants.

application<sup>7</sup>, it finds applications in FRP because of its high combustion efficiency even at low pressure and temperature.

Boron has the greatest advantage of having much higher heat of combustion than *Al* or *Mg* (next to *Be*) and is a highly attractive fuel for ram-rocket engines<sup>7</sup> (air/fuel ratio, 11). Another advantage of boron is that its combustion products do not dissociate easily. In high performance rocket ramjets endothermic dissociation of combustion products increases with Mach number, leading to decrease in combustion temperature and consequently lower performance. Bayer Chemie has planned test firing of *B*-based integrated ram-rocket engine which may give  $I_{sp}$  of over 1000 s<sup>8</sup>. However, high melting and boiling points of *B* (2450 and 3931 K respectively) cause serious ignition and combustion

efficiency problems. Further, *B* is highly reactive, and a boron oxide ( $B_2O_3$ ) layer is formed on the surface of boron particles<sup>8,9</sup>. Moreover, *B* is much harder than *Al* and its abrasive qualities could cause processing problems in extruded propellant charges as well as severe erosion of the exhaust nozzle. The acidity and the porous nature of sub-micron *B* cause undesirable high viscosity during the mixing process. These are major problems in the development of a practical propulsion system based on *B*.

Beryllium is also recommended in various hybrid and ram rockets<sup>8,9</sup>. However, *BeO* (main combustion product) is highly toxic. Beryllium also requires special equipment and facilities for manufacturing and handling<sup>8,10</sup>. Zirconium on the other hand, although expensive, highly sensitive to electrostatic discharge and pyrophoric in nature, has higher density leading to higher volumetric  $I_{sp}$ . Additional advantage of *Zr* is the ease in ignition even at higher loading. Zirconium is therefore emerging as a potential component of FRP<sup>8</sup>.

### 3. OXIDISERS

Ammonium perchlorate (AP) is a commonly used oxidiser for fuel-rich compositions. King<sup>3</sup> reported HMX-based fuel-rich compositions with higher performance and found improvement in ignitability of HMX-based formulations by incorporating minor quantities of AP (5-10 per cent). Ammonium nitrate (AN) is used in FRP, where high rate of gas generation is essential. Sodium nitrate (SN) also finds applications due to its high density (2.26 g/cc), oxygen availability, heat of combustion and affinity of its exhaust species with ram air<sup>11</sup>. King<sup>3</sup> used organic acids and fluoro compounds as oxidisers.

### 4. BINDERS

Polybutadienes are the preferred choice as binder for FRP among various polymeric binders. The major advantages of polybutadienes are: superior structural integrity, high load bearing capability, clean crosslinking reaction and high fuel value<sup>12</sup>. During recent times, azide polymers like glycidyl azide polymer (GAP) and BAMO/NMMO copolymer are emerging as potential energetic binders for FRP<sup>13,14</sup>. The most important attribute of azide polymers is positive heat of formation (28-42 kcal/mol), which results in exothermicity during binder degradation. On the

contrary, decomposition of polybutadienes is an endothermic process, thereby adding to heat sink effect. The BAMO/NMMO copolymer-based fuels have both advantages and disadvantages. The main advantages are vigorous pyrolysis resulting in high combustion efficiency and higher performance at lower air-to-fuel ratios as it contains certain fraction of oxygen and thus requires less ambient oxygen to burn. The disadvantage is lower performance at normal solid fuel ramjet (SFRJ) operating conditions due to lower heats of reaction (lower hydrocarbon content in comparison with conventional hydrocarbon fuels), despite their high positive heats of formation. However, the difference in performance between these two types of fuels becomes much smaller in terms of volumetric  $I_{sp}$ , which is very important for volume-limited propulsion systems<sup>14</sup>. Double base (DB) binders, capable of exothermic decomposition, are recommended to achieve sustained combustion<sup>15</sup>. King<sup>3</sup> has reported teflon, polyvinylidene fluoride and derlin as binder system for pressed Mg-based compositions. Hydrocarbons, like naphthalene are also useful in this respect. Naphthalene sublimates at low temperature, and combustion affinity of exhaust species with ram air helps in ejecting out the condensed particles through nozzle<sup>11</sup>.

## 5. METAL COMBUSTION

Fundamental character of metal combustion process is expected to be unaltered in propellants, including air breathing ram rockets. The combustion behaviour of metals is influenced by thermochemical characteristics

as well as the physical properties, like ratio of molar volumes and coefficient of thermal expansion of the solid metal/metal oxide and solubility of metal oxide in molten metal. Details regarding combustion characteristics of potential metal components are reported by various researchers<sup>6,7,9,14,16</sup>. Thermochemical and physical characteristics of metals used in FRP are given in Table 1.

## 6. COMBUSTION OF METALLISED PROPELLANTS

Metals tend to form agglomerates at the propellant surface due to low burn rates of FRP, resulting from low oxidiser content. It has been observed that agglomeration diminishes, if (i) metal ignition occurs rapidly on exposure to the combustion gases, (ii) fine size of the oxidiser is incorporated and (iii) oxygen-rich flame is situated close to the burning surface<sup>17</sup>. It is reported that oxidiser-binder decomposition and interactions produce nonequilibrium combustion temperature  $T^*$ , which decides whether metal will melt or ignite. Fuel-richness reduces the environmental temperature during propellant combustion below the ignition point (*Al* and *Be*). However, the replacement of binder by metal raises<sup>18</sup>  $T^*$ . Some of the typical formulations and their ballistics reported by various researchers are given in Table 2.

### 6.1 Al/Mg-Al-based FRP Compositions

Price<sup>19</sup> has reviewed the findings on combustion of aluminised propellants. Most representative description

Table 1. Physical and thermochemical characteristics of metal fuels

Metal	Metal		Metal-Oxide		Volume ratio (oxide/metal)	Oxide sp. heat of formation (kcal/g)	Air/ fuel ratio	Specific gravity
	MP,K	BP,K	MP,K	BP,K				
<i>Li</i>	454	1620	1700	3200	0.52			
<i>Mg</i>	923	1381	3075	3350	0.81	5.92	3.29	1.74
<i>Al</i>	932	2740	2318	3800	1.45	7.42	4.44	2.70
<i>Be</i>	1556	2750	2823	4123	1.68	15.89	8.89	1.89
<i>Si</i>	1685	3582	1883	3000	–	7.77	5.69	2.33
<i>Ti</i>	1950	3550	2128	4100	1.73	4.69	3.34	4.51
<i>Zr</i>	2125	4650	2960	5200	1.45	2.87	1.76	6.44
<i>B</i>	2300	3950	723	2550		14.07	11.12	2.35
<i>Ni</i>	1728	3093	2257		–			8.90

of combustion of *Al* is depicted in Fig. 2. In the propellant microstructure, small *Al* particles fill the space among larger oxidiser particles. Each particle experiences temperature rise as it approaches the propellant burning surface (the thickness of the thermal wave in the propellant is comparable to the diameter

of the *Al* particle). As the surrounding binder material pyrolyses away, the emerging particle is exposed to a vapour atmosphere that consists initially of fuel species. The particle projects increasingly from the binder, but is retained on the surface by a 'wet' layer of binder and its intermediate decomposition products. Stuck to the

Table 2. Fuel-rich formulations studied by various researchers

Sl No.	Formulation	Burn Rate (mm/s)	$T_f$ (K)	$I_{sp}$ (s)	A/F (Ratio)	Surface Temperature (°C)	Ref
	HTPB/AP/Al (17.3-12.5/81.4-57/10-30)	3.6-4.6 (18-53 KSC)				853 (at 30 % level)	27
2	HTPB/AP/Al (30/20/50)	-		600-800			23
3	HTPB/AP/Al (60-30/20-50/20)	6.4-2.1 (at 70 KSC)					26
4	HTPB/AP/Al/Mg (17/50/20/30)	5-7	2400		2.8	-	50
5	HTPB/AP/Mg (15.6-12.1/73.3-57/10-30)	4.03-5.95 (18-53 KSC)				641 (at 30 % level)	27
6	HTPB/AP/Mg-Al (20/60-45/20-35)	10.2-6 (at 70 KSC)					26
7	HTPB/AP/Mg (25/25/50)	0.2-0.4 (5 KSC)	1895*		5		31
	HTPB/AP/Mg (25/60-50/15-25)	7.5-8.6 (at 70 KSC)					26
	HTPB/AP/HMX/Mg	0.33-0.95 (at 70 KSC)					
	NaNO <sub>2</sub> /Mg (20-60/80-40)	26-58.6		-		-	28
	HTPB/B (60/40)	-	-	15000-8750**	-	260	14
	CTPB/AP/B (30/50-30/20-40)	1.5-7 (1.5-10 KSC)	2600-2750	450/ 900-1200	5/15		36
13	POLY (BAMO/NMMO)/B (60/40)	1.05 (at 10 KSC)	-	12500- 7500**	-	760 <sup>§</sup> 260	14
14	Zr/AP/HTPB (20-60/60-20/20)	6.4-2.3 (at 70 KSC)		-			45
15	Zr/AP/DB matrix (20-40/20-0/60)	16.9-15 (at 70 KSC)					45
16	Zr/AP/DB matrix [GAP](20-40/20-0/60)	29-25 (at 50 KSC)					45
17	AP/PB composite	3 (at 6 KSC)		600			
18	Double base composition	2 (at 6 KSC)		575			13
19	GAP-based fuel	20 (at 6 KSC)	2000	750			13
20	GAP-based formulation (fuel)	5-25	2500 (5 Mpa)	800		1465 (at 50 KSC)	13

\* @ 4500 KNS/m<sup>3</sup>, \*\* Volumetric Specific Impulse KN/M<sup>3</sup> at equivalent ratio 1 and 2 atm, respectively

§ combustion product temperature

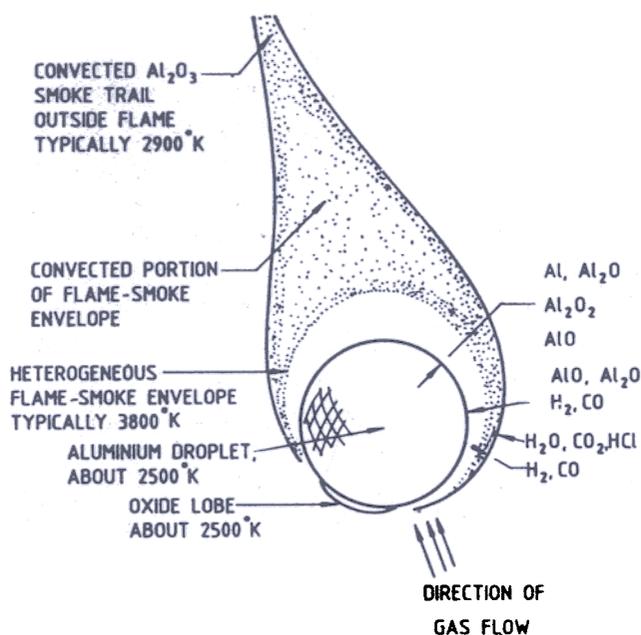


Figure 2. General nature of the combustion zone of an aluminium droplet burning in a mild convective flow.

surface (or still immersed in the pyrolysing melt), the particle is joined by the other emerging particles, thus experiencing an accumulation or concentration process leading to ill-defined clumps described as 'agglomerates'. This is evidenced by several studies on decomposition and pyrolysis of the binders as well as study of quenched burning surfaces. As the propellant burning surface continues to regress, the adhering *Al* particles experience a transition in the chemical and thermal environment, resulting from combustion of neighbouring and underlying oxidiser particles which leads to sufficient breakdown of the oxide skin to allow coalescence of each accumulate into one or more agglomerates. The agglomeration event is usually indistinguishable from the event of ignition and may occur either on the burning surface or after detachment<sup>19</sup>. A variety of simplified tests in controlled atmospheres have yielded data that can be correlated by the relation,  $T = kD^n/a^{0.9}$ , where  $T$  is the burning time,  $D$  the initial droplet diameter, and  $a$  the mole fraction of oxidising gas in the atmosphere. Typical agglomerates require 5-50 ms to burn, which means that a significant portion of the combustor volume is occupied by burning agglomerates<sup>19</sup>.

Wood<sup>20</sup> found that particle size of metal also plays an important role; 5  $\mu\text{m}$  *Al* particles get ignited at the

propellant surface whereas larger particles are ignited only after leaving the surface. Addition of small particles to coarse material shortened the ignition lag. Sambamurthi *et al*<sup>21</sup> found that wide oxidiser particle size distribution produces larger agglomerates. Pai Vernekar *et al*<sup>22</sup> found that in pressed *AP/Al* pellets, maximum burn rate is obtained at intermediate metal content. Tsujikado<sup>23</sup> reported sustained combustion of aluminised composition with *Al* up to 50 per cent and *HTPB/AP* in 60/40 ratio.

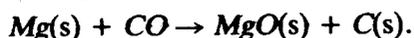
Friedman and Macek<sup>15</sup> reported that *Al* combustion may be improved by various methods, such as use of (a) binder capable of exothermic decomposition, like *DB* binder, (b) combination of *Al* with *Mg* which is reported to raise  $T^*$  to a value where efficient *Al* combustion can take place and (c) coating of *Al* with *Mg*. Kuehl and Glassman<sup>24</sup> have also suggested that the formation of a protective oxide coating on metal can be prevented by amalgamating the particle surface. Northan and Sullivan<sup>25</sup> reported improvement in combustion efficiency of low burning rate for *Al* propellant by mixing 2 per cent *Mg* in the form of *Mg-Al* eutectic alloy. John<sup>26</sup> obtained superior burn rates for *Mg-Al*-based compositions than *Al*-containing propellants (metal content 20-50 per cent, fine *AP* 30-60, *HTBP* 20 per cent) and found copper chromite as an effective catalyst.

Hardt and Brewster<sup>27</sup> carried out quench collection and burn rate studies on *Al* and *Mg/Al* metallised composite propellants and suggested that metal needs to be heated to higher temperature before igniting, leading to heat sink effect which decreases burn rate by robbing energy from the primary oxidiser-binder flame. However, a compensating heat feedback (reactive and conductive) is produced by the combustion of the metal. The enhancement magnitude depends upon agglomeration characteristics. Smaller agglomerates release energy close to the surface leading to increased conductive feedback. The radiative heat feedback is less dependent on agglomeration characteristics. At low metal concentration, burn rate increases and with metal content >20 per cent heat sink effect is large enough leading to decrease in burn rate. At 10 per cent metal content unagglomerated particles (20  $\mu\text{m}$ ) outnumber agglomerated particles (100-200  $\mu\text{m}$ )<sup>27</sup>. As metal content increased to 20 per cent both the numbers were equal and at 30 per cent metal level,

agglomerated particles were in larger fraction. Alloy particles gave higher burn rates than *Al*-containing particles, which may be due to lower ignition temperature and stronger conductive heat feedback for *Mg*. Aluminium tends to release more of its energy farther away from the surface, resulting in significant radiative, but little conductive heat feedback. As radiation is much less pressure dependent than conduction, aluminised propellants become increasingly pressure insensitive with increase in metal content. The pressure exponent for *Mg/Al* composition remains more or less same at different metal levels. Hardt and Brewster<sup>27</sup> have also correlated the theoretical surface temperature with the values computed from burn rate data and computed heat feedback of 186-389 K for the propellants based on *Al* and 241-515 K for those containing *Mg-Al*.

## 6.2 *Mg*-based Compositions

King<sup>3</sup> has studied *Mg*-based cast/pressed systems based on NC/HTPB binder and AP/nitramine oxidiser systems. His main finding is an efficient after-burn characteristic of *Mg*-based cast compositions as compared to *B* and *Al*-containing compositions, even under adverse conditions. King suggested that *Mg* vapours, produced in exhaust streams of the primary motor, react violently with oxygen, producing oxygen atom, thereby promoting vigorous ignition and combustion with all fuel species. He found on the basis of thermodynamic calculations, that even high *Mg* loadings (50 – 60 per cent) give high primary chamber temperatures (>2000 K), implying that these formulations would burn well and give good primary ejection. King has also reported increase in theoretical volumetric heating value on increase in *Mg* loading. However, primary motor temperature was nearly independent of *Mg* loading up to about 50-55 per cent due to highly exothermic reaction:



At higher loadings, *CO* is exhausted and primary motor temperature decreases drastically on further increase in *Mg* content. Thus, according to King's findings the maximum practical *Mg* content in *Mg-AP* formulations is about 60 per cent. At this loading, theoretical volumetric heating values are approximately 8.454 kcal/m<sup>3</sup>.

Singh *et al*<sup>28</sup> evaluated propellant compositions based on *Mg* with 20-60 per cent SN and observed an

increase in burn rate with oxidiser content up to 30 per cent. Further increase in oxidiser content led to fall in burn rate. They found magnesium nitride ( $\text{Mg}_3\text{N}_2$ ) as one of the combustion products up to 30 per cent oxidiser content and claimed that with more than 30 per cent SN, the molten oxidiser envelops the reactive metal surface, producing inert environment, thereby reducing the heat released in condensed phase due to oxidation of *Mg*. Jain and Oommen<sup>29</sup> investigated thermal ignition behaviour of *Mg* in a mixture containing AN along with organic fuels and found that a composition with *Mg* content as high as 25 per cent ignited at low temperature (<145 °C), when mixed with the appropriate organic fuel, which by themselves are not ignitable with AN. Among other metals (*Al*, *Ni*, *Fe*, *Sn*, *Zr* and *Cu*), *Zr* appears to be close to *Mg*. Liljegren and Anderson<sup>30</sup> have reported that *Mg*-based (up to 50 per cent) FRP containing up to 30 per cent AP should stable combustion in presence of a combustion catalyst. Wimmerstorm and Lundgren<sup>31</sup> found that 2 per cent  $\text{Fe}_2\text{O}_3$  doubles the regression rate of composition with *Mg* (50 per cent), AP (25 per cent), and HTPB (25 per cent). During recent times, *Mg-NaNO*<sub>3</sub>-naphthalene-based compositions have evinced interest due to their self-pyrolysing capability. It has been found that increase in fuel richness leads to improvement in performance. However, it is necessary to maintain SN level more than 20 per cent and *Mg* content less than 65 per cent to ensure efficient combustion. An  $I_{sp}$  of 600 s is reported for an optimised composition<sup>11</sup>.

## 6.3 Boron-based Formulations

A schematic description of physico-chemical processes occurring during combustion of *B*-based FRP with poly BAMO/NMMO binder is given by Hsin *et al*.<sup>14</sup>, depicting processes occurring in four zones, namely, (i) inert heating zone, (ii) subsurface reaction zone, (iii) first-stage combustion zone, and (iv) second-stage combustion zone, as well as the temperature and product profiles of various zones as reported by King<sup>32</sup> and Faeth<sup>33</sup> (Fig. 3). When *B*-weight is low (< 20 per cent), the *B/B*<sub>2</sub>*O*<sub>3</sub> particles can reach the second-stage ignition temperature of 1900 K, and a high amount of heat release is obtained due to efficient *B* combustion. The heat feedback to the burning surface increases and burn rate is enhanced by the increase of *B* content in the FRP. However, as *B* content exceeds

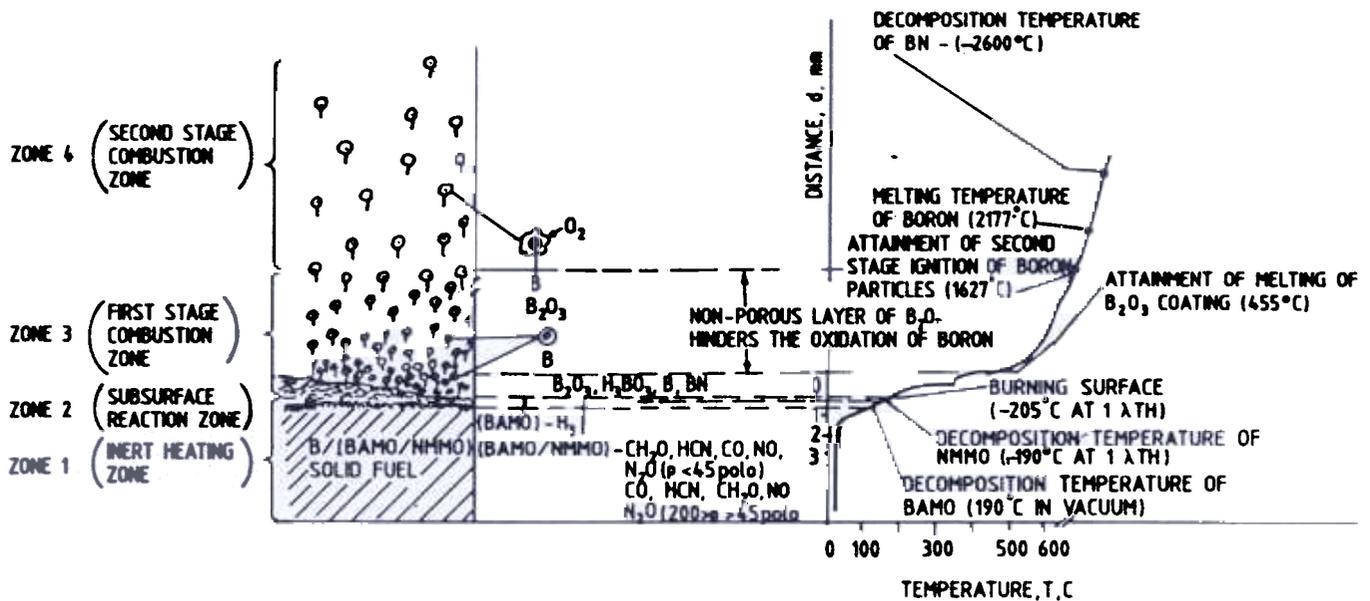


Figure 3. Physico-chemical processes in the combustion of boron/poly (BAMO/NMMO) solid fuel in air.

20 per cent, the energy sink effect becomes a dominant factor in reducing the heat feedback to the burning surface. This reduction is either due to the unattainment of the second-stage ignition temperature or the extension of the active reaction zone to a much farther distance from the burning surface. This hypothesis is confirmed by thermocouple measurements.

Murphy<sup>34</sup> suggested that conductive, convective and radiative heat transfer between *B*-based propellant constituents and their combustion products contributes towards the combustion and found that *B* burns only if the particle size is extremely small or combustion temperature is extremely high. Lichmann<sup>35</sup> has described a set-up for combustion studies of boron-based slurries in a ram burner using fast two-colour pyrometer to measure particle temperature and IR (0.2–14.5  $\mu\text{m}$ ) to determine exhaust temperature from *OH* bands. He has reported the exhaust plume temperature of 2500 K for *B*. Kubota and Miyata<sup>36</sup> studied FRP gas generator with *B* content of 20–40 per cent and AP content of 30–50 per cent in CTPB binder (30 per cent) and found an increase in theoretical  $I_{sp}$  with increase in *B* content as well as air/fuel ratio (*E*). Theoretical  $I_{sp}$  for a composition with 40 per cent *B* at an *E* value of 40 comes to 1400 s and  $T_f$  reaches 2770 K at an *E* value of 5. Increase in *B* particle size (2.7–9  $\mu\text{m}$ ) led to decrease in burn rates and pressure index. Combustion efficiency ( $\eta_c^*$ ) increased from 79–91 per cent, when multiple port was used instead of single port,

or particle size of *B* was reduced. *E* had relatively little effect on combustion efficiency.

Snyder *et al*<sup>37</sup> studied pyrolysis and ignition behaviour of *B*-HTPB and *B*-BAMO/NNMO solid fuels for ramjet applications, using  $\text{CO}_2$  laser as controlled external energy source, and found reduction in ignition delay till *B* content increased up to 20 per cent. Increase in delay time was observed on further increase in *B*-loading (30 and 50 per cent). Inclusion of *Mg*, *Mg-Al* alloy and cerium fluoride (10 per cent) led to decrease in delay time. The ignition process in case of both the fuels was found to begin in gas phase and then the reaction zone propagates towards the surface of the condensed phase. Energetic binder enhances ignition and combustion of *B*. Thus, the pyrolysed product velocity for BAMO/NNMO copolymer was much higher than HTPB (1000 and 30 cm/s respectively). Laredo and Gany<sup>38,39</sup> studied the combustion of propellants containing large percentage (40–50 per cent) of metal additives by using high speed photography technique in conjunction with high pressure window strand burner and observed that propellant combustion is irregular and regression rate varies about 1/3 to 3 times of the average value in case of *B*-based systems. Marci<sup>40</sup> has claimed improvement in injection efficiency of *B*-containing FRP by incorporating 50 per cent *B* as agglomerate. Folsom<sup>41</sup> reported a high energy fuel made by 30–35 per cent *B* isomer/*Be*/*Li* (1  $\mu\text{m}$ ) and 5–30 per cent *Li* or beryllium perchlorate. Mastwerdt and Selzer<sup>42</sup>

reported that ignition temperature of *B* could be lowered from 2500 to 800 K by using  $LiB_{2.5}$  compound obtained from their co-melt. As *Li* continues to vapourise or lithium borate was formed, there was no possibility of closed oxide layer formation. This system has great potential in air-augmented propulsion devices.

#### 6.4 Beryllium-based Compositions

Beryllium, like *Al* poses ignition and combustion problems in FRP. Metals, the oxides of which form a low-melting eutectic with the oxides of base metals, are reported to be effective in achieving reduction of ignition temperature, if used for coating. Thus, *Be* coated with *Al* gives a mixed oxide melting at around 685 °C (much lower than the melting point of *BeO* alone which is 2550 °C)<sup>43</sup>. Ignition of *Be* is also reported to be improved by high water vapour content, probably due to the formation of a porous oxide/hydroxide mixture on the surface instead of a protective oxide film<sup>44</sup>. Because of toxicity of its combustion products, much interest has not been evinced in *Be*-based formulations as ramjet fuel.

#### 6.5 Zirconium-based Formulations

Limited information is available for *Zr*-based formulations. The present authors studied<sup>45</sup> the combustion behaviour of *Zr*-based propellants and found that *Zr* powder-incorporated systems have superior burn rates than aluminised compositions. Highly metallised (40 per cent metal content in DB matrix and 60 per cent metal content in HTPB binder) systems with *Zr* gave stable combustion in the pressure range of 50-90 KSC, unlike corresponding *Al*-containing compositions. Compositions with DB matrix gave much higher burn rates than HTPB-based formulations and incorporation of the polymer binder GAP in DB matrix led to two-fold increase in burn rates in almost all the cases. Lou *et al*<sup>46</sup> have patented FRP having 80-90 per cent *Zr* (particle size, 2-4  $\mu\text{m}$ ) and AP in 10-20 per cent binder. They claimed achievement of high burn rates and low burn rate sensitivity by controlling particle size distribution. Reed *et al*<sup>47</sup> reported an improved *Zr*-based ramjet fuel, using hydroxy and carboxy terminated fluorocarbon binders. Harry<sup>48</sup> has developed high gas-producing fuel containing 60-90 per cent AN and 10-40 per cent *Zr*.

### 7. THEORETICAL PREDICTION

Kubota and Kuwahara<sup>49</sup> have discussed the

applicability of burn rate-pressure relationships for current solid propellants to FRP. Zhongqin *et al*.<sup>50</sup> have described equations used for computing thrust,  $I_{sp}$  and combustion efficiency. King<sup>3</sup> has discussed application of thermodynamic relationships to compute heating value and flame temperature of *Mg* and *B*-based FRP. Devpaul<sup>11</sup> applied NASA SP-273 computer code to theoretically predict thermodynamic properties (enthalpy and equilibrium temperature) as well as to determine mass fractions of *Mg* (vapour and liquid), magnesium oxide (solid), *C* (solid), *Na* (vapour),  $H_2$ ,  $N_2$  in constant pressure equilibrium combustion products for self-pyrolisable *Mg-NaNO<sub>3</sub>*-naphthalene-based compositions.

### 8. CONCLUSION

A review of the combustion studies of metallised FRP brings out that the ideal performance is not achieved with the current systems based on *Al* and *B* because of low combustion efficiency. The problem is more critical particularly at low pressure used in upper stage motor. Owing to anomalous burning and heat transfer effect in the current systems, the condensed phase material (metal and oxides of metal) puddles and flows during the applications involving high acceleration. Further, the details regarding the combustion process of metallised FRP are not yet available to define the mechanism clearly. Zirconium and *Ti* appear to have potential to offer FRP with efficient combustion. Energetic polymers, like GAP can be used as binder/plasticiser to achieve superior combustion efficiency. Detailed research is needed to develop FRP having all the three important attributes, namely, ease of ignition, stable combustion under operating conditions and high performance  $I_{sp}$  in a single composition. This may be possible by arriving at a judicious combination of two or more metal fuels and selection of a suitable energetic binder.

### REFERENCES

1. Thomas, A.N. (Jr). *Astronautics & Aeronautics*, June, 36-41.
2. Boyars, C. & Klager, K. *Advances in chemistry-series 88*. American Chemical Society, Washington D.C., 1969.
3. King, M. Atlantic Research Corporation, Virginia Report No. TR-PL-5520, 1976.

4. Langer, H. & Goedtke, P. Fr. Demande Fr 2, 565, 583 (Cl. CO6 B21/00), 13 December 1985, DE Appl. 3, 321, 196, 11 June 1983, 9 pp.
5. Sanden, R. *Aerospace Rep.*, 1983, **21**, 16 Abstr No. N 83-27055.
6. Summerfield, M. & Krier, H. *Aerospace and Mechanical Sciences Rep.* AMS 1968, 84, 22.
7. Rastogi, R.P. & Deepak, D. *J. Sci. Industr. Res.*, 1977, **36**, 470-90.
8. Mama, H.P. *Int. Def. Rev.*, 1988, 291-95.
9. Glassman, I. *ARS Progress in Astronautics and Rocketry: Solid propellant rocket research.* Academic Press, New York, 1960, I, 253-57.
10. Lean, V.F. US Dept. Commerce Office Tech. Service, 1961, AD, 260, 268.
11. Devpaul, G. Regional Engineering College, Warangal, India, Report No. 4, 1987.
12. Terry, V.O. & Hara, M.A. *Chem. Abstr.* 1986, 93, 10383 m.
13. Kubota, N.; Yano, Y.; Miyata, K.; Kuwahara, T.; Mitsuno, M. & Nakagawa, I. *Propellants, Explosives, Pyrotechnics*, 1991, **16**, 287-92.
14. Hsin, W.; Peretz, A.; Te Huang, I. & Kuo, K. *J. Propulsion*, 1991, **7**(4), 497-504.
15. Friedman, R. & Macek, A. Proc. International Symp. on Combustion, 1963, **9**, 703-12.
16. Letwin, T. & Wojcick, S. *Arch. Procesow Spalania*, 1974, **5**(4), 447-59.
17. Cohen, N. S. *Amer. Inst. of Aero. & Astro.*, 1969, **7**(7), 1345-52.
18. Beal, J.L.; Brown, W.R. & Vassallo, F.A. *Pyrotechnics*, 1965, **3**, 135-60.
19. Price, E.W. Fundamentals of solid propellant combustion. *Amer. Inst. of Aero. & Astro.* Publication, 1984.
20. Wood, W.A. *ARS progress in astronautics and rocketry: Solid propellant rocket research.* Academic Press Inc., New York, 1960.
21. Sambamurthi, J.K.; Price, E.W. & Sigman, R.K. *Amer. Inst. of Aero. & Astro.*, 1984, **22**, 1132-38.
22. Pai Vernekar, V.R.; Deevi, S. & Deevi, S.C. *Combustion & Flame*, 1987, **67**, 163-73.
23. Tsujikado, N. *Kogyo Kayaku*, 1979, **40**(4), 313-18.
24. Kuel, D. K. & Glassman, I. *US Patent* 3, 328, 805, 1967.
25. Northam, G. B. & Sullivan, E. M. *NASA Tech. Note*, NASA, Washington D.C., 1973, 11 pp. NASA TN D-7133.
26. John, T. Poona University, Pune, 1988, M.Sc. thesis.
27. Hardt, B.E. & Brewster, M.Q. 25th JANNAF combustion meeting, Huntsville, Alabama, 1988, **1**, 199-205.
28. Singh, H.; Somayajulu, M.R. & Bhaskara Rao, R. *Combustion & Flame*, 1989, **76**(1), 57-61.
29. Jain, S.R. & Oommen, C.J. *Therm. Anal.*, 1989, **35**(4), 1119-28.
30. Liljegren, T. & Anderson, B. NTIS from Sc. Tech Aerospace Rep., 1980, **18**(8), Abstr. No. N 80-17245; Report FOA-C-20299-DI, 1979, 22 pp.
31. Wimmerstorm, P. & Lundgren, R. Proceedings of 22nd International Conference of ICT, 2-5 July 1991, at Karlsruhe Germany (Paper Nos. 96/1 - 96/7.)
32. King, M.K. *Space Rockets*, 1982, **19**(4), 294-306.
33. Faeth, G.M. Proc. 21st JANNAF Combustion Meeting, 1984, CPIA Publication 412, **1**, 15-29.
34. Murphy, J.M. Proc. 3rd Int. Heat Transfer Conf., Chicago, 1966, **1**, 321-30.
35. Lichmann, W. *Propellants, Explosives, Pyrotechnics*, 1992, **17**, 14-16.
36. Kubota, N. & Miyata, K. Papers presented to the 22nd International Annual Conference of ICT, Germany, 1991, (Paper Nos. 37/1-37/7).
37. Snyder, S. T.; Chen, D. N.; Fatherolf, B. L.; Litzinge, T. A. & Kuo, K. Proc. 15th JANNAF Combustion Meeting, 1988, **1**, 219-30.
38. Laredo, D. & Gany, A. *Isr. J. Technol*, 1983, **21**/1-2, 91-95.
39. Laredo, D. & Gany, A. *Acta Astronautica*, 1983, **10**/5-6, 437-41.
40. Marci, B.J. US Patent 3, 986, 909, 1976.
41. Folsom, E.D. US Patent 3, 130, 097, 1961.
42. Mastwerdt, R. & Selzer, H. *Amer. Inst. of Aero. & Astro.*, 1976, **14**(1), 100-02.
43. Kuehl, D. K. US Patent 3, 381, 473, 7 May 1968; *Chem. Abstr.*, 1968, **69**, 20837.

- 44 Kuehl, D.K. *Amer. Inst. of Aero. & Astro.*, 1965, 3, 2239.
- 45 Athawale, B.K.; Asthana, S.N.; Shrotri, P.G. & Singh, H. Combustion studies composite based propellants. The XIIIth National Conference on Internal Combustion Engines and Combustion, 1994. 338-45.
- 46 Lou, R.A.; Kotzakian A. (Jr) & Burket, S.C. US Patent 3, 761, 330, 1973.
- 47 Reed, R. (Jr); Brudette, G.W.; Mayer, G.W. & Vuono, L.R. US Patent 319, 159. NITS Order No. PAT-APPL-6-319159, 1982.
- 48 Harry, A. US Patent 2, 954, 284. 1960.
- 49 Kuboita, N. & Kuwahara, T. *Propellants, Explosives, Pyrotechnics*, 1991, 16, 51-54.
- 50 Zhongqin, Z.; Zhenpeng, Z.; Jinfu, T. & Wenlan, F. *J. Propulsion*, 1986, 2(4), 305-10.