Effect of metal and metal hydride additives on combustion characteristics of composite solid propellants

R K Deepachanthiran, K Gnanaprakash*
Indian Institute of Technology, Hyderabad
Hyderabad, Telangana, India

1 Introduction

Composite solid propellants (CSPs) play a vital role in propelling solid rocket motors (SRMs). It is a mixture of various chemical ingredients, like an oxidizer, binder, and metal additives [1]. Many research studies were done on adding metal additives to CSPs in the past, which helped in enhancing the energetic performance of CSPs. Among the metal additives aluminum (Al), magnesium (Mg), iron (Fe) or boron (B) are often added to CSPs to increase the energetic performances like specific impulse and heat release.

The influence of these metal particles has been constantly studied in the CSPs since they improve the burning rate of CSPs, which is in demand for various applications. Al is one of the commonly used metal additives in CSPs because of its high performance, easy availability, and good stability [2,3]. Many studies have been done using the aluminized solid propellant. When Al particles are added in nano size to CSPs, they increase the burning rate by two times compared to that of propellant without Al particles [4,5]. Even though these Al particles help in enhancing the burning rate of CSPs, these particles tend to form agglomerates during combustion. When these agglomerates pass along with the exhaust gases, they lead to two-phase flow losses, thereby reducing the velocity of the gaseous products and in turn the thrust generated by SRMs. The overall combustion efficiency of SRMs will also be affected by these agglomerate particles [6,7].

Mg is one of the alternative metals that is added as a metal additive to CSPs. In comparison to Al, the energy density of Mg is lower, but it has lower melting and boiling point as well as better ignition performance. They have higher reactivity, which results in vapor combustion mode [8]. Also, the oxygen consumption for combustion is also less compared to Al [9-11]. The other advantage of adding Mg particles in CSPs is that it can reduce HCl composition in the exhaust products. The HCl product formation is decreased as the Mg-based fuel forms MgO during combustion, which later forms magnesium hydroxide ($Mg(OH)_2$) while in contact with water in exhaust gases. Even though the addition of Mg particles in CSPs have some advantages over Al particles, it produces less specific impulse and combustion temperature.

The utilization of metal hydrides as additives in CSPs has been gaining interest due to their potential to enhance energy performance while reducing metal agglomeration. The addition of metal hydrides in CSPs delivers higher theoretical specific impulse, which is predicted to improve the burning rate. This study examines the combustion performance of CSPs incorporating metal hydrides, specifically lithium aluminum hydride ($LiAlH_4$) and lithium boron hydride ($LiBH_4$). The burning rate of these CSPs are compared with those containing conventional metal additives like Al and B. In this work, CSPs were formulated with nano-Al, micro-Al, and micro-Mg particles, and their burning rates were measured. This research emphasizes the influence of metal and metal hydride additives in CSPs.

Correspondence to: gnan@mae.iith.ac.in

2 Experimental Details

2.1 Propellant preparation

The ammonium perchlorate (AP), used as the oxidizer, is obtained from Tamil Nadu Chlorates, Madurai, India. The purity of the AP is 99%, and it does not contain any anticaking agents. The oxidizer particles are used in bimodal size distribution (Bi AP), with fine AP particles ranging from 44 to 75 microns and coarse AP particles ranging from 300 to 400 microns. The Al particles are obtained from Vedayukt, Jharkhand, India. Aluminum metal particles are used in two sizes, which are micro and nano size. The binder is made up of Hydroxyl terminated polybutadiene (HTPB) cured by toluene diisocyanate (TDI), with the addition of di-octyl adipate (DOA). The monomodal AP based propellants contain 80% total solids loading and 20% binder system, while the bimodal AP based propellants contains 86% total solids loading and 14% binder system. The metal particles are added at 15% by weight of total propellant for metal additives and 20% by weight for metal hydride additives, by replacing equivalent weight of oxidizer particles.

HTPB and DOA were measured accurately with 1% error, according to the composition weight percent and were mixed for 5 minutes, followed by the sequential addition of metal additives. The ingredients are hand mixed thoroughly for 30 minutes with addition of AP. The mixture was degassed in a vacuum chamber for 1 hour. TDI was added for curing as the last ingredient, and the propellant was left to cure in a hot-air oven at 60°C for 7 days. Continuous load is applied on the propellant loaded in a casting chamber to ensure minimal void. After the propellant is cured, it is cut into 5mm x 5mm x 10mm (L x W x H) dimension pieces. Ignition is achieved through nichrome wire along the top of the sample which was connected to DC power source.

2.2 Experimental setup

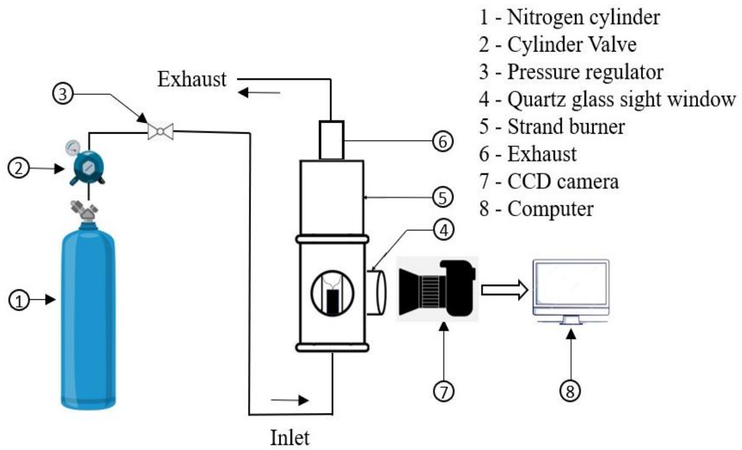
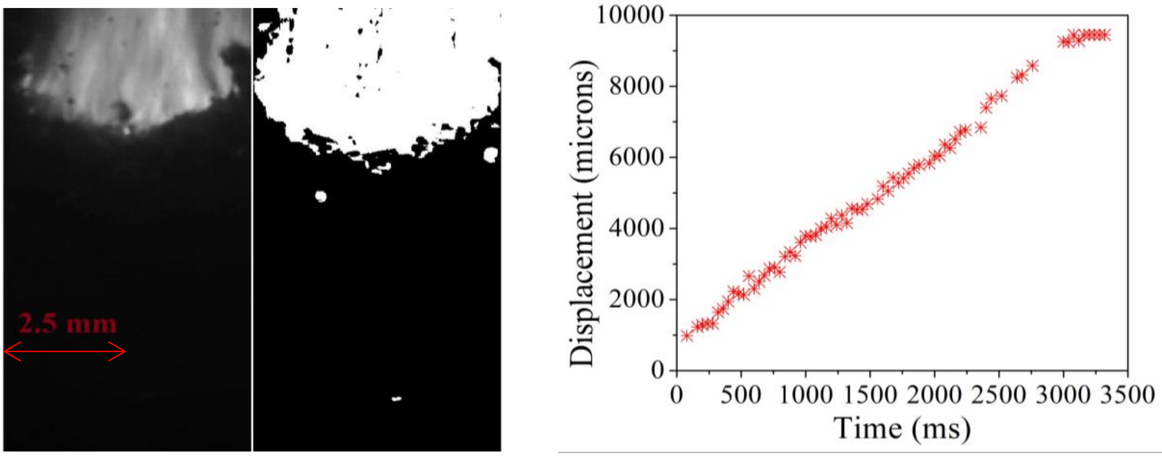


Figure 1 Schematic diagram of strand burner

A windowed strand burner is used for the burning rate measurement. It is a stainless steel (SS) chamber, capable of withstanding high pressures. It has two quartz glass along the circumference of the chamber. Combustion photography is the process that is used to estimate burning rates of CSPs. Using quartz glass, the combustion event of the propellant being burned is captured using a charged-coupled device (CCD) camera (Allied Vision Prosilica GT) at a framing rate of 25 fps, coupled with a Nikon lens of variable aperture. The setup also consists an inlet for pressuring the chamber using nitrogen gas and an outlet for releasing gas and flumes from burned propellants. The sample is placed on the pedestal and kept inside the chamber. Sample is coated with a thin layer of silicon grease on the side faces (except front side which faces the camera) to inhibit side burning of the propellant sample. Nichrome wire is connected between the electrodes and kept on the top face of the propellant sample. The entire chamber was properly sealed and purged with pure N_2 each time before and after the experiments. Ignition was achieved using a DC power source which is connected to the outer end of electrodes.

Combustion event of the propellants is acquired using a CCD video camera and stored in computer. A variable neutral density filter is attached in the camera to reduce the intensity of the flame image based on the type of propellant sample being burned. Camera calibration is done before each set of experiments to ensure a constant magnification factor while calculating burn rate. Figure 2(a) shows the original image and its binarized version, processed using MATLAB software, illustrating propellant combustion. Bright side denotes the burned region or area and the dark side denotes the unburned region or area. The line that separates the bright and dark area is the location of flame front and it is stored. The images of the combustion event are viewed frame by frame and the flame front location is marked along a straight vertical line in each frame. The time interval between each frame is 40 ms. A MATLAB code is used to determine the burning rate. The displacement of flame front in each frame is plotted against the framing time with a correlation coefficient > 99%. A dataset is removed if more than half of the displacement points are eliminated from the locus point. A sample dataset of displacement vs time graph is shown in Fig. 2 (b). The slope of the straight line will provide the burning rate of the propellant. All the experiments were repeated two times for repeatable results. The error that is involved in this measurement is ± 0.05 mm/s.



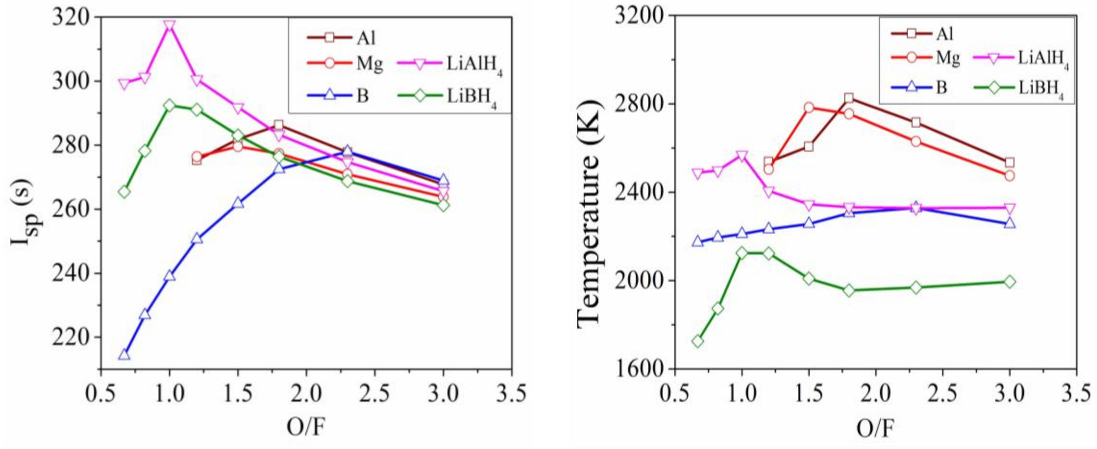
(a) (b)

Figure 2 (a) Original and binarized image of propellant combustion (b) Displacement vs time interval

3 Results and Discussion

3.1 Thermo chemical equilibrium analysis

The rocket performance for different metal content were calculated theoretically using NASA chemical equilibrium analysis (CEA) software [13,14]. Calculation are performed with pressure of 70 bar, exhaust supersonic area of 40, rocket equilibrium temperature of 3800 K and shifting equilibrium through nozzle. The combination of propellant formulations from AP/Metal/HTPB (75/5/20) to (40/40/20) are tested.



(a) (b)

Figure 3 (a) Variation of Specific impulse with O/F ratio for different metal and metal hydrides and (b) Variation of Temperature with O/F ratio for different metal and metal hydrides.

An essential parameter for the performance analysis of rockets is specific impulse (I_{sp}). Higher the value of I_{sp}, lower the amount of propellant is required for the rocket to produce same amount of thrust. The specific impulse result from the CEA analysis is shown in Fig. 3 (a). Peak I_{sp} for Al-based propellant is attained at oxidizer-to-fuel ratio (O/F) of 1.8 while for Mg-based propellant, it occurs at 1.5. As Al particles has more energy density and higher heat of combustion than Mg, Al-based propellant composition shows higher I_{sp} compared to Mg-based propellant composition. At lower O/F ratio, the higher amount of boron content in the propellant reduces the availability of oxidizer, leading to incomplete combustion. From the CEA analysis results, it shows that $LiAlH_4$ and $LiBH_4$ propellant produces higher I_{sp} compared to standard metalized propellant with their peak I_{sp} attained at even lower O/F ratios. During combustion, the metal hydrides decompose into their constituent metals and H_2, which contributes to increase in I_{sp}.

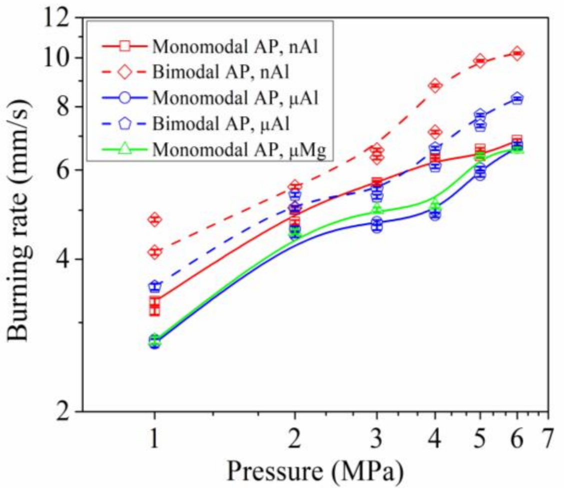
A higher the adiabatic flame temperature indicates more thermal energy is available for conversion into kinetic energy. Fig. 3 (b) shows the temperature trend for the propellant formulation with various metal and metal hydride. The peak temperature for Al-based propellant is attained at 1.8 O/F ratio while for Mg-based propellant, it attained at 1.5 O/F ratio. As boron have high melting and boiling point, it make the propellant to produces lower flame temperature. Also, a significant amount of the heat is absorbed by boron particles for their transition from solid to gas. As metal hydrides have high content of hydrogen, it leads to produce lower flame temperature. At high temperature, hydrogen dissociates into hydrogen atom. During this process, thermal energy is absorbed, thereby reducing overall flame temperature [15]. In case of $LiBH_4$, both H_2 and boron particles absorbs heat energy during the combustion. So, they produce very lower flame temperature compared to other metal and metal hydrides. From the CEA results, it shows that metal hydrides have greater potential for improving the combustion performance of CSPs.

3.2 Burning rates

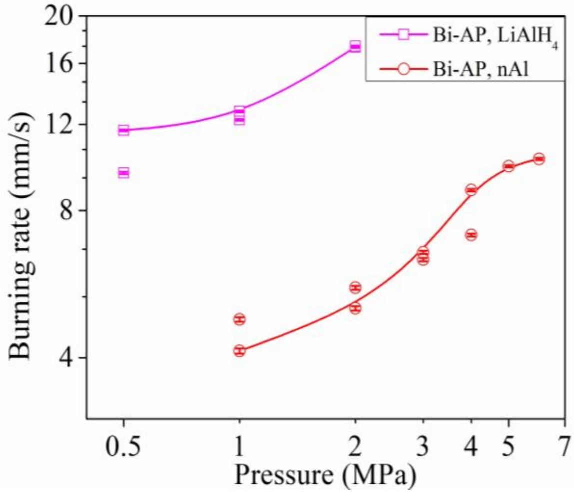
The burning rate of three different metal-based propellants was tested at six different pressures, with each experiment repeated two times. The measured burning rate for monomodal AP based CSPs with micro-Al, micro-Mg and nano-Al samples were 6.43 mm/s, 6.04 mm/s and 6.4 mm/s respectively whereas for bimodal AP based CSPs with nano-Al and micro-Al were 9.86 mm/s and 7.33 mm/s at 5 MPa pressure. The burning rate was observed to be increasing with an increase in pressure, as the burn rate equation is pressure-dependent. Experimentally it is concluded that the propellant containing nano-

Al exhibits higher burning rate compared to other metal-based propellants. As nano-Al particles have a higher surface area-to-volume ratio than micron sized particles, it enables them to react quickly with oxidizer and release more heat on the propellant burning surface. These results were similar to those of previous studies [4] on propellants containing nano-Al.

The effect of oxidizer particle size on the burning rate, is evident in the experimental results presented in Fig. 4 (a). The propellant composition that are based on monomodal size distribution of oxidizer tends to produce lower burning rate compared to those with bimodal AP based propellants. This reduction in burning rate is because of the use of single-sized, relatively larger oxidizer particles, which reduces the packaging efficiency of the propellant [16]. In contrast, bimodal AP based propellants, which consists of both coarse AP (cAP) and fine AP (fAP), shows improved combustion performance. The fAP particles, which have higher surface area ratio, decomposes rapidly thus enhancing heat feedback to the propellant surface. Moreover, these fAP occupy the interstitial spaces between cAP particles, thereby improving the packaging density as well as combustion efficiency. Furthermore, the addition of nano-Al particles contributes to an increased burning rate of the propellant through ignition of these particles by the leading-edge flames (LEFs) over the coarse AP/binder interfaces [17]. These LEF is the main heat feedback for the propellant surface thus promotes rapid ignition of nano-Al particles.



(a)



(b)

Figure 4 (a) Burning rate of propellant containing nano-Al, micro-Al and micro-Mg additives (b) Comparison of burning rate of propellant with $LiAlH_4$ and nano-Al particles.

Micro-Al based propellant (monomodal and bimodal AP) exhibits similar result to previous studies [4]. As discussed earlier, the bimodal AP based micro-aluminized propellant shows higher burning rate compared to monomodal AP based propellant. Although aluminum particles of all sizes possess the same heat of combustion, micro-Al particles have a significantly lower surface area compared to nano-Al particles, resulting in reduced reactivity and, consequently, a lower burning rate. Also from the experimental results, monomodal AP based micro-Al and micro-Mg propellants exhibit similar burning rates. These results were similar to the previous studies [12] on propellants containing Al and Mg. Although Mg particles have lower energy density compared to Al metal, there are two reasons for the comparable or slightly higher burning rates in some pressure ranges for micron scale: (i) Mg particles have a lower ignition point, making them easy to ignite and burn, (ii) Mg particles react quickly in an oxygen or nitrogen environment, releasing heat. As a result, the burning of propellant containing micro-Mg is either similar to or slightly higher than those propellant containing micro-Al.

The experimental results of $LiAlH_4$ based propellant were presented in Fig.4(b) along with nano-Al based propellants. The propellant formulation consists of an AP/$LiAlH_4$/Binder ratio of 60/20/20. Upon decomposition, $LiAlH_4$ produces LiH, Al particles and large amount of hydrogen gas. The presence of both Al and H gas contributes to increasing the flame temperature and promotes combustion. Consistent with the CEA predictions, $LiAlH_4$ based propellants exhibits significantly higher burning rate compared to both nano-Al or micro-Al based propellants. The measured burning rates are ~17 mm/s at a pressure of 2 MPa, which is 210% higher than nano-Al and 245% higher than micro-Al propellants. However, at higher pressures, the propellant begins to show sign of structural disintegration due to large content of metal hydrides. This is because of the low thermal stability of $LiAlH_4$ particles, which compromises the mechanical integrity of the propellant under elevated pressures.

In summary, the theoretical result shown in Fig. 3, indicates that hydride-based propellants produce the highest I_{sp} at O/F ratio of around 1, whereas conventional metalized propellants produce their peak I_{sp} at O/F ratio of 1.8. This suggests that a higher amount of fuel can be carried in the rockets relative to oxidizer. Also from the results, it is shown that propellant with metal hydrides can produce a higher burning rates, and higher I_{sp} compared to standard metalized propellants. From the burning rate measurements, the propellant containing nano-Al particles produces higher burning compared to micro-Al and micro-Mg propellants. Future work, will focus on exploring the effects of adding B, $LiAlH_4$ and $LiBH_4$ particles of various loading in CSPs and comparing its combustion performance (burning rate) with Al-based propellants.

4 Conclusion

In this work, the theoretical I_{sp} for metal and metal hydride propellants were calculated using NASA CEA analysis. The results shows that propellant containing metal hydrides produces the highest I_{sp}. Among these, $LiAlH_4$ produces the highest I_{sp} of 317.6 s at O/F ratio of around 1. However, hydride-based propellants produce lower flame temperature compared to metalized propellants due to their higher hydrogen content. During combustion, these hydrogen molecules absorb heat to dissociate into hydrogen atoms. From the experimental results, the effect of micro-Al, micro-Mg, and nano-Al, $LiAlH_4$ particles in CSPs at six different pressures were examined, and it shows an increase in burning rate as pressure increases. Propellant with $LiAlH_4$ particles exhibit a significantly higher burning rate of ~17 mm/s, outperforming Al, and Mg-based propellants. Future work will focus on the experimental investigations under extended higher-pressure conditions. Additionally, further studies will explore the effect of incorporating B, $LiAlH_4$ and $LiBH_4$ particles with various metal loadings in CSPs. The performance of these propellants will be analysed against Al, Mg and B-based propellants.

References

[1] Sutton GP, Biblarz O. (2017) Rocket Propulsion Elements, John Wiley and Sons (ISBN 9781118753651)

[2] DeLuca LT (2018) Overview of Al-Based Nanoenergetic Ingredients for Solid Rocket Propulsion. Def. Technol. 14: 357.

[3] Trunov, M. A., Schoenitz, M., & Dreizin, E. L. (2005). Ignition of aluminum powders under different experimental conditions. *Propellants, Explosives, Pyrotechnics: An International Journal Dealing with Scientific and Technological Aspects of Energetic Materials*, *30*(1), 36-43.

[4] K. Jayaraman, K.V. Anand, D.S. Bhatt, S.R. Chakravarthy, R. Sarathi (2009) Production, characterization, and combustion of nano-aluminium in composite solid propellants, J. Propuls. Power 25, 471–481.

[5] Rai, 0., Park, K., Zhou, L., & Zachariah, M. R. (2006). Understanding the mechanism of aluminium nanoparticle oxidation. *Combustion theory and modelling*, *10*(5), 843-859.

[6] Q. Yan, X. Zhang, H. Li, Z. Song, M. Liu (2011) Oxidation process of aluminum powder in solid propellant and influence factors on its combustion efficiency, Chem. Propel. Polym. Mater. 9. 20-26.

[7] Yuan, J., Liu, J., Zhou, Y., Wang, J., & Xv, T. (2019). Aluminum agglomeration of AP/HTPB composite propellant. *Acta Astronautica*, *156*, 14-22.

[8] Law, C. K., & Williams, F. A. (1974). Combustion of magnesium particles in oxygen-inert atmospheres. *Combustion and Flame*, *22*(3), 383-405.

[9] Shen, C., Yan, S., Yao, J., Li, S., Guo, X., Nie, J., ... & Jiao, Q. (2021). Combustion behavior of composite solid propellant reinforced with Al-based alloy fuel. *Materials Letters*, *304*, 130608.

[10] Liu, L., Ao, W., Wen, Z., Wang, Y., Long, Y., Liu, P., ... & Li, L. K. (2022). Modifying the ignition, combustion and agglomeration characteristics of composite propellants via Al-Mg alloy additives. *Combustion and Flame*, *238*, 111926.

[11] Wei-qiang, P. A. N. G., Xue-zhong, F. A. N., & Hui-xiang, X. U. (2013). Characteristics of B/Mg compounds and the effect on the burning rate properties for fuel-rich propellant. *Journal of Solid Rocket Technology*, *36*(3), 363-367.

[12] Ishihara, A., & Brewster, M. Q. (1993). Combustion studies of boron, magnesium, and aluminum composite propellants. *Combustion science and technology*, *87*(1-6), 275-290.

[13] Gordon, S., & McBride, B. J. (1994). *Computer program for calculation of complex chemical equilibrium compositions and applications. Part 1: Analysis* (No. NAS 1.61: 1311).

[14] Gordon S, McBride BJ, Zeleznik FJ. (1996). *Computer program for calculation of complex chemical equilibrium compositions and applications Part II*. USA: Report RP1311.

[15] Maggi, F., Gariani, G., Galfetti, L., & DeLuca, L. T. (2012). Theoretical analysis of hydrides in solid and hybrid rocket propulsion. *international journal of hydrogen energy*, *37*(2), 1760-1769.

[16] Kubota, N. (2015) Combustion of Composite Propellants. u: Propellants and Explosives, Weinheim, Germany: Wiley, : 195-252.

[17] Jayaraman, K. (2008). Production and characterization of nano-aluminium and its effects in solid propellant combustion, Ph.D. Thesis, Department of Aerospace Engineering, Indian Institute of Technology Madras, Chennai, India.