Radiant Ignition of Solid Rocket Propellants for Space Propulsion

L.L. Rossettini, D. Orsini, L. Galfetti, and L.T. De Luca
SPLab, Dipartimento di Energetica, Politecnico di Milano, I-20156 Milan, Italy

Abstract

The ignition delay was investigated of innovative solid rocket propellants of interest for space propulsion. These are formulations, based on a standard matrix of Ammonium Perchlorate and HTPB binder, with different metallic additives. A CO_2 laser apparatus was used for testing ignition, with simultaneous high-resolution and high-speed visualization of the incipient flame. In this paper, preliminary results on the effects of AlH_3 and MgH_2 hydrides, potentially useful for both solid and hybrid rocket propulsion, are reported. With respect to a preselected reference metallized formulation, the tested compositions based on metal hydrides feature a reduced ignition delay.

Keywords: Aluminum Hydride, Magnesium Hydride, solid propellant, ignition delay, space propulsion

Introduction

During last decades space activities have been expanding, especially due to commercialization of space products such as multipurpose satellites and low-gravity research and development. Improved propulsion systems are requested by both governmental and industrial parts to effectively decrease launch costs. Moreover, in recent years, strong demands for green propellants emerged. On one hand, specific impulse increases are directly linked with mass saving and costs decreases. On the other hand, low-cost and green propellants show lower performance than the standard ones. In this scenario, new technologies were tested and old ones are being updated, from hybrid propulsion assuring operational safety and a potentially clean operative environment, to solid propulsion resorting to new additives for augmented performance. Although hybrid propulsion promises very attractive technology, solid propulsion still assures the simplest engine architecture, lowest cost, and widest availability. Many efforts on improving solid propellants were taken, both towards low cost and environmentally clean composite materials, and also towards high-energy additives. Metal hydrides, tested at laboratory scale in ammonium perchlorate (AP)-based solid propellants, revealed good performance in terms of ballistic behavior, pressure dependence, and combustion efficiency [1].

Solid propellant ignition and ignition phenomena in general were investigated for many years [2][3][4]. Consistent correlations and results were obtained for conventional AP-based solid rocket propellants [5]. Pressure, geometry, composition effects were studied since the ‘60s [1][6][7][8]. However, in most applications, the metal fuel used was just aluminum in micrometric size. The results of decades of research on the ignition of AP-based composite propellants can be summarized in the plot of Figure 1, reporting experimental data for aluminized and nonaluminized formulations from a variety of international sources [9].

Metal hydrides are very promising additives for solid propellants. They offer both low molar mass due to hydrogen content and quite good density compared to regular metal powder. If properly prepared [1] metal hydrides are chemically stable under ambient conditions for long time. Theoretical predictions and ballistic properties of aluminum hydride based solid propellants were reported in [1], but no results could be found in the open literature on ignition trends. In order to acquire a comprehensive understanding in this area, a comparative investigation is now carried out on radiant ignition of propellants with different percent and type of metal hydrides.

Motivations and objectives

MgH_2 and AlH_3 (or alane) are well-known reducing agents potentially usable in several applications, from hydrogen storage to polymerization catalysis. They can be successfully utilized both in solid and hybrid rocket propulsion: the combination of high energy release due to metal oxidation and low molecular mass due to hydrogen content provide optimum propulsive performance [1]. However, metal hydrides, especially alane, present a strong sensitivity to oxidation and hydration, low thermal stability, friction sensitivity and potential hazards during and after manufacture. Stabilized AlH_3 was previously tested and safely used at SPLab [1], however, alane is not yet industrially produced [10], with the exception of Russia, at the moment the only large-scale producer of high-quality stabilized alane. On the other hand, MgH_2 is widely available at affordable price.

The ultimate goal of this study is to characterize new high-energy compositions for space applications, by replacing the standard micrometric aluminum with metal hydrides in the conventional HTPB binder / Al formulation for either solid or hybrid propulsion. In this respect, it should be noted that HTPB is not the ideal binder for AlH3 [1].

Physical and chemical characterization

AlH_3 and MgH_2 are relatively similar fuels of low density (1.477 gcm^{-3} and 1.450 gcm^{-3} respectively) but large molecular mass (30.01 $gmol^{-1}$ for AlH_3 and 26.32 $gmol^{-1}$ for MgH_2). Even if their density is quite less than aluminum (2.70 gcm^{-3}), they offer high density for hydrogen storage, from about 8% hydrogen by mass for MgH_2 to about 10% for AlH_3, hence providing a higher density of hydrogen (0.148 gcm^{-3} for AlH_3 and 0.116 gcm^{-3} for MgH_2) than liquid hydrogen (0.071 gcm^{-3}) [11]. Bulk AlH_3 tends to dehydrogenate at room temperature in a few hours, but the alpha phase of alane (α-AlH_3) has been observed to be stable while rapid dehydrogenation occurs at temperatures in the range 180-190 °C [12]. MgH_2 instead, is quite stable at room temperature and tends to dehydrogenate at much higher temperature than alane, in the range 380-450 °C [13][14][15][16]. Moreover, magnesium has slightly lower melting point and heat of fusion than aluminum.

Thermochemical calculations show that replacing Al by the corresponding AlH_3 results in both a lower flame temperature and a lower average molecular mass of the combustion products [1]. Overall, an increased specific impulse of about 20 s is found by comparing the two optimized formulations (AP/HTPB/Al vs. AP/HTPB/AlH3) [17]; detailed analyses of MgH_2 influence on specific impulse and adiabatic flame temperature investigations were not found in the literature. AlH_3 addition was shown to bring a substantial gain for hybrid and solid rocket motors, especially for the upper stages of space launchers [18]. Comparative analyses of ignition and combustion for solid propellants containing metal hydrides were not found in the literature.

Dehydrogenation process occurs at different temperatures for the two metal hydrides. Both reactions are endothermic (11.3 $kJmol^{-1}$ for AlH_3 [19] and 75 $kJmol^{-1}$ for MgH_2 [20]) at standard temperature and pressure. Krier et al. [11][16][21] experimentally investigated the dehydrogenation process velocity for AlH_3 using a shock tube. A two-step mechanism is assumed to occur for dehydrogenation of the two metal hydrides as:

Dehydrogenation:	$AlH_3 \rightarrow Al + 3/2$ H2	$MgH_2 \rightarrow Mg + H_2$
Oxidation:	Al + ¾ O2 → ½ Al2O3	$Mg + ½ O_2 \rightarrow MgO$

where the MgH_2 mechanism suggests formation of MgO because the activation energy barrier for H_2 desorption in vacancy containing MgH_2 (1.02 eV) is much lower than that in pure MgH_2 (3.30 eV) [22].

Experimental

Experimental procedure

Ignition delay measurements and flame structure visualizations were conducted, under 0.1 and 0.5 MPa of nitrogen, for radiant flux from about 30 to 100 Wcm^{-2}. As an externally applied energy of known intensity, thermal radiation represents an effective tool for investigations of solid propellant ignition and burning mechanisms. The effects of low (5% and 10%) and high (15% and 23%) mass fractions of metal hydrides were assessed by comparison with a reference metallized formulation well known to SPLab. The detailed compositions of the tested solid propellant samples are shown in Table 1.

Table 1: Tested solid propellant formulations

	Reference (Metallized)	**5%AlH3**	**10%AlH3**	**15%AlH3**	**23%AlH3**	**5%MgH2**	**15%MgH2**
Oxidizer	AP	AP	AP	AP	AP	AP	AP
Binder	HTPB	HTPB	HTPB	HTPB	HTPB	HTPB	HTPB
Metal additive	18% Al	05% AlH_3	10% AlH_3	15% AlH_3	23% AlH_3	05% MgH_2	15% MgH_2

Propellant samples (4.5 x 4.5 x 10 mm) of the formulations under examination were burned in a nitrogen-flushed window bomb in order to measure the ignition delay. Ignition is performed by a 10.6 µm CO_2 laser in a pressurized combustion chamber kept at constant pressure by a pneumatic servo-mechanism. A power meter (response time < 0.5 ns) is used to monitor the radiant flux emitted from the laser source. Either first flame appearance or go/no-go ignition data are collected, by both a visible light photodiode and high-speed videocamera. These two pieces of information, properly combined, allow a good understanding of the transient flame structure of the innovative formulations under the explored operating conditions. At least 5 samples were tested for each experimental point; for each sample several ignition delay readings were performed using two different acquisition systems, according to well-established SPLab procedures. All collected data were treated with the Chauvenet criterion [23] and errors computed on a standard deviation basis.

Experimental results

Ignition delay curves are plotted in bi-logarithmic scales in Figure 2. Formulations with low metal hydrides content ignite quicker than the reference metallized propellant at both pressure levels. Although higher percent of hydrides feature more data scattering, a slightly decrease on ignition delay is detectable, especially at 0.5 MPa. Comparing formulations with same percent of metal hydrides, one can note that samples with 5% alane ignites quicker than the ones with 5% of magnesium hydride (Figure 2 upper left). However, this behavior seems to revert for samples with higher hydrides content (Figure 2 upper right). The observed ignition boundary slopes are reported in Table 2. Only the reference metallized propellant shows an increase of the slope (absolute value) with pressure, in agreement with other findings; see for example [24][25].

The results of decades of research on the ignition of conventional AP-based composite solid rocket propellants can be summarized in the plot of Figure 1, reporting experimental data for aluminized and nonaluminized formulations from a variety of international sources. An essential agreement is found in the competent literature for compositions with microaluminum addition over the usual range 0-20 % mass fraction of metal [11].

Super-imposing the results obtained with the metal hydrides formulations show the interesting results described by Figure 3. The reference metallized propellant data are consistent with the aluminized formulation plotted in Figure 1. Adding micrometric aluminum to the propellant increases the ignition delay: this is probably due to the increased thermal responsivity of the metallized condensed-phase, shifting the ignition temperature to higher values with respect to non metallized compositions.

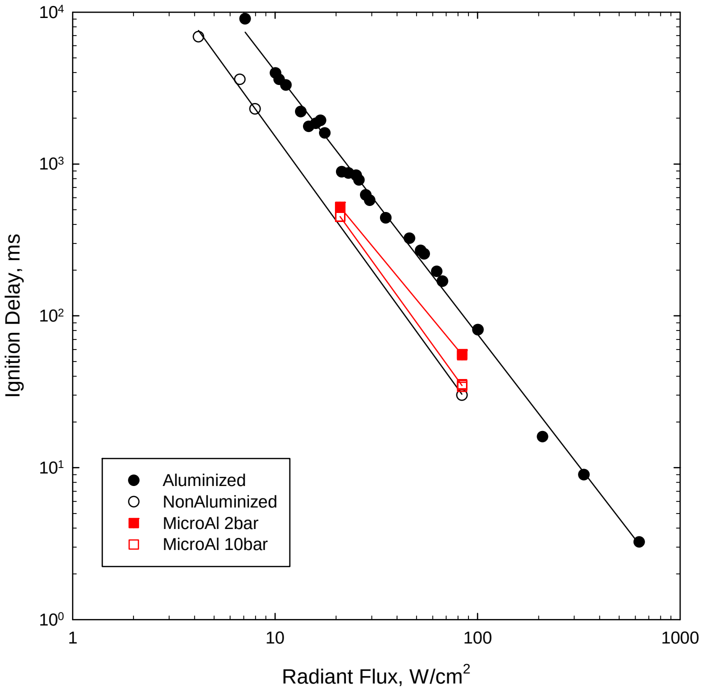

Figure 1: Ignition delay of conventional aluminized and nonaluminized AP-based composite solid rocket propellants [26].

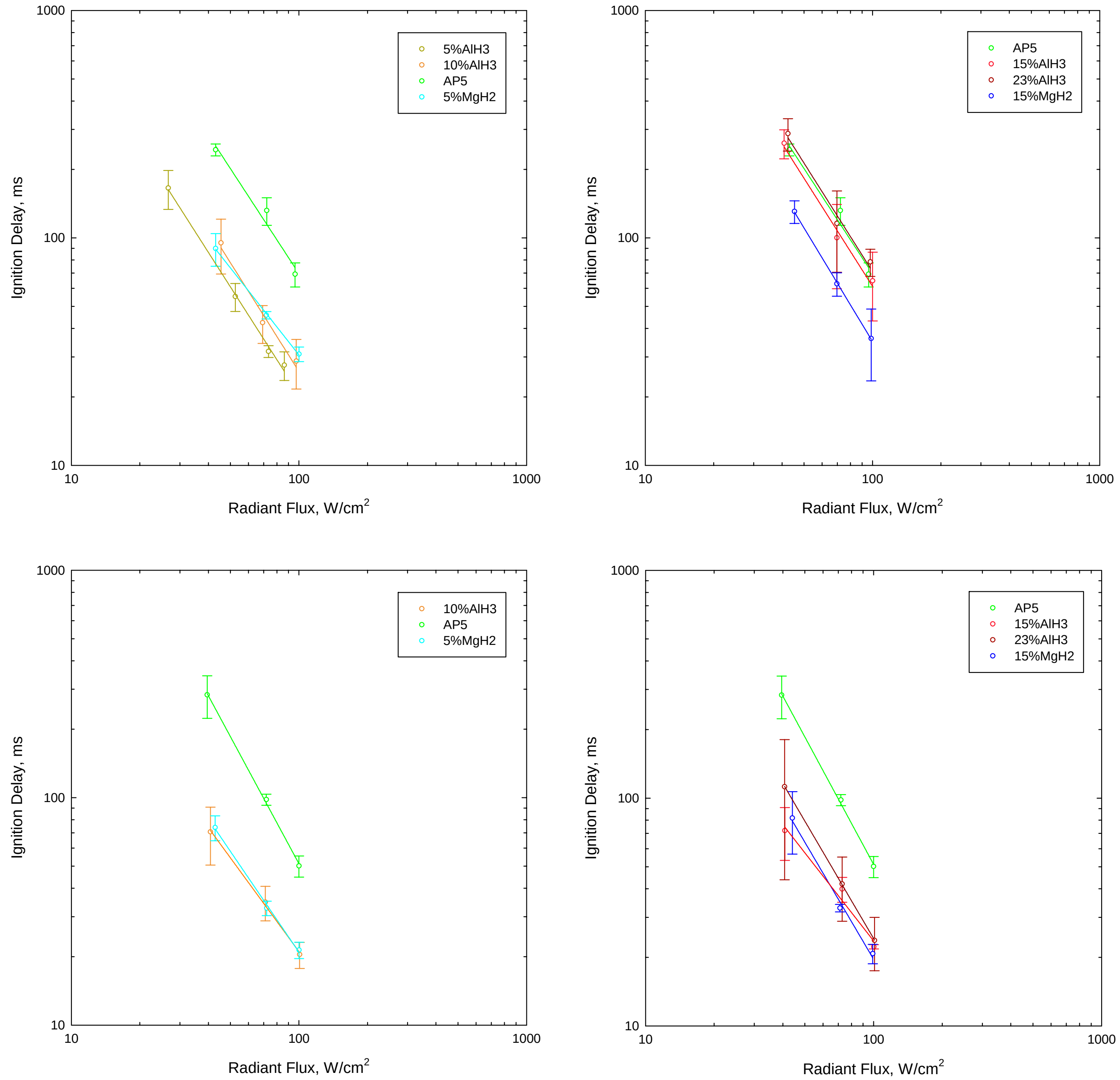

Figure 2: Ignition delay results for low (left) and high (right) metal hydride contents at 0.1 MPa (upper) and 0.5 MPa (lower) nitrogen pressure

The ignition boundary slopes of the metal hydrides samples are similar to the values reported in the literature for aluminized and non aluminized propellants. However, low hydride mass fractions strongly decrease the time required to reach a self-sustained ignition (up to 62% less) at 0.1 MPa. High hydrides mass fraction tend to push the slope to the upper limit curve for aluminized HTPB-based propellants, confirming the increased thermal responsivity effect due to metal addition. However, ignition delay is still slightly reduced with respect to the reference formulation (up to 48% for magnesium hydrides samples and just to 8% for aluminum hydrides ones). Thus, hydrogen release by the tested metal hydrides yields faster ignition only for small mass fraction of the hydrides. In comparing the two hydrides, the different temperature required to release hydrogen should be taken into consideration. Work is in progress to identify a well defined mechanism.

Increasing pressure to 0.5 MPa implies a positive influence for both low and high hydrides content samples. For the high percentage samples, the reduction of ignition delay is pretty marked, up to 50-63% for both hydrides.

In Table 2 the experimental ignition boundaries slopes are reported for different pressure levels. Essential agreement is found with other studies reported in literature for double-base propellants [24], AP-PBAN-Al formulations [26] and HMX based propellants [28].

Table 2: Comparing ignition boundary slopes

Formulation	**Slope**	
	0.1 MPa	**0.5 MPa**
Standard non Al	-1.84 ± 0.05	
5%MgH2	-1.27 ± 0.03	-1.47 ± 0.07
15%MgH2	-1.66 ± 0.03	-1.70 ± 0.15
5%AlH3	-1.57 ± 0.07	-
10%AlH3	-1.59 ± 0.24	-1.37 ± 0.07
15%AlH3	-1.57 ± 0.17	-1.28 ± 0.19
23%AlH3	-1.58 ± 0.20	-1.71 ± 0.02
Reference Al	-1.53 ± 0.25	-1.86 ± 0.07
Standard Al	-1.74 ± 0.02	

Incipient flame investigation

The incipient flame evolution was investigated with a visible light photodiode. Digital, color high-speed movies of the flame on-set were taken and compared with photodiode light intensity signals. For metal hydrides, one can expect a lower ignition time and hence temperature with respect to the corresponding metal fuel, yielding an increased burning rate and decreased pressure dependence. Replacing Al with AlH_3 was shown to sensibly decrease the pressure exponent in the burning rate law [1]. Dehydrogenation frees H_2 which burn at the surface of the hydrides-based compositions, while the evolved Al is subjected to distributed burning in the post-flame gases [1].

Flame evolution during ignition shows different behavior depending on formulation type but not on ingredients percentage (Figure 4). While the reference aluminized propellant flame evolves slower and with big sparks of light intensity, magnesium hydrides based propellants show a quicker and much more nervous evolution in terms of light emission. Aluminum hydrides based propellants feature the steepest and also more regular light intensity curves, probably due to a better combustion process [1]. Likely, this is due to the higher temperature required by magnesium hydride to decompose and free the hydrogen. Notice that in Figure 4 ignition of the reference aluminized formulation seems to anticipate the other compositions at 1 bar, but this instance is due to scattering in the experimental data collection. The signals acquired and plotted in these diagrams were selected in correspondence with the high-speed movie frames reported in Figure 5.

Digital, color, high-speed movies taken at SPLab show a very clean flame for both hydrides compositions. The quality of the flame structure looks superior to that of the reference aluminized formulation (Figure 5). The radiative flame intensity from AlH_3 based samples is sensibly lower than both the reference aluminized and magnesium hydrides formulations. By increasing pressure (Figure 5, from g to l) a small increase in luminosity is detected, but the basic flame structure is maintained.

Assuming that H_2, freed during AlH_3 dehydrogenation phase, reacts very close to the surface, it is possible to suppose that amorphous aluminum burns almost completely in the reaction zone and little aggregation/agglomeration process occurs [1]. Recalling its sensibly larger dehydrogenation temperature, different mechanisms may be acting for the “cloudy” flame structure of magnesium hydride based formulations. More investigations are needed to understand the difference in flame development.

High-resolution and high-speed video recording was performed on aluminum hydrides based samples. Aggregation/agglomeration mechanism is evident and similar to that occurring in the reference aluminized propellant (Figure 6).

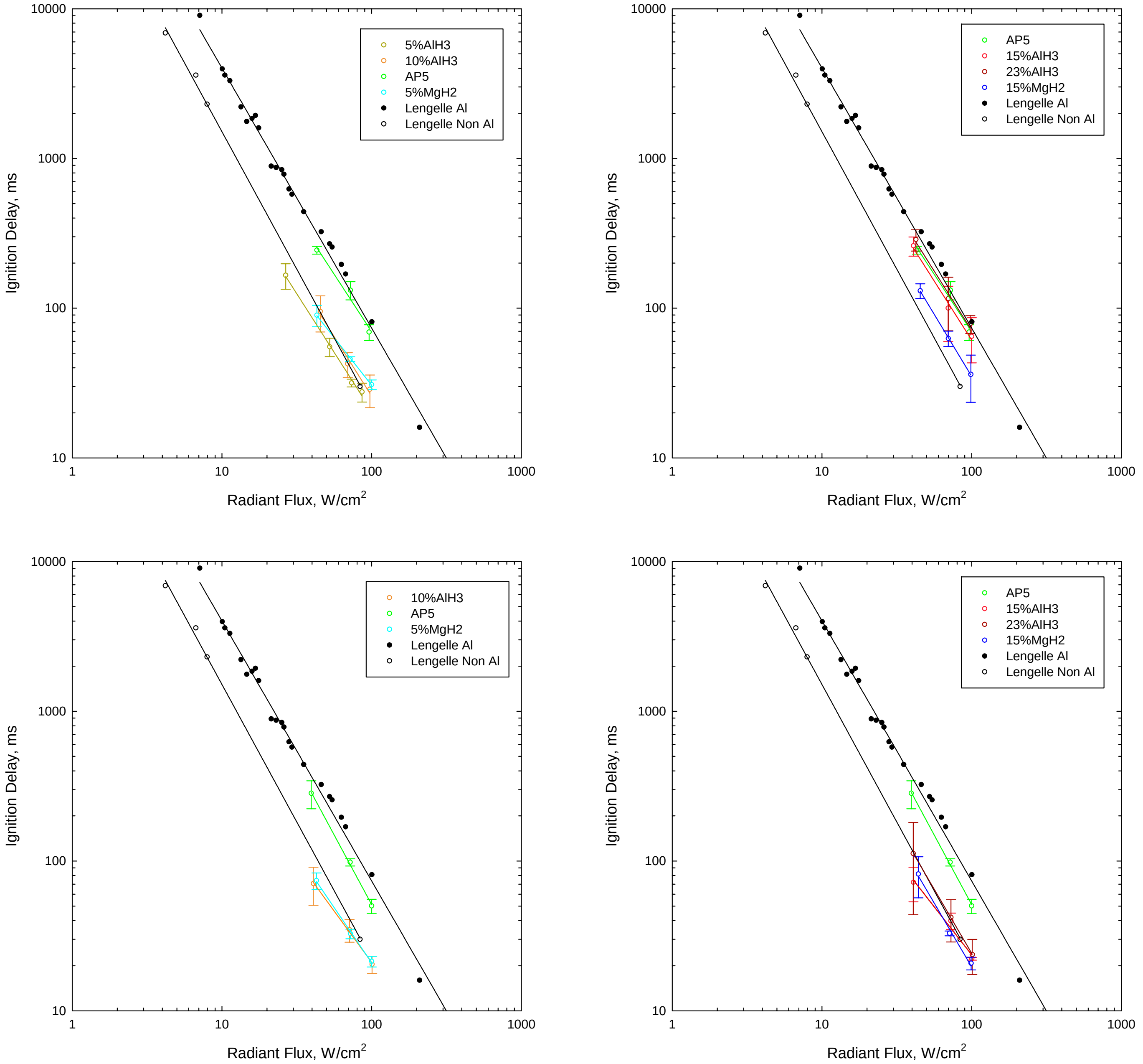

Figure 3: Ignition delay for low (left) and high (right) metal hydride contents at 0.1 MPa (upper) and 0.5 MPa (lower) nitrogen pressure compared with literature data [11]

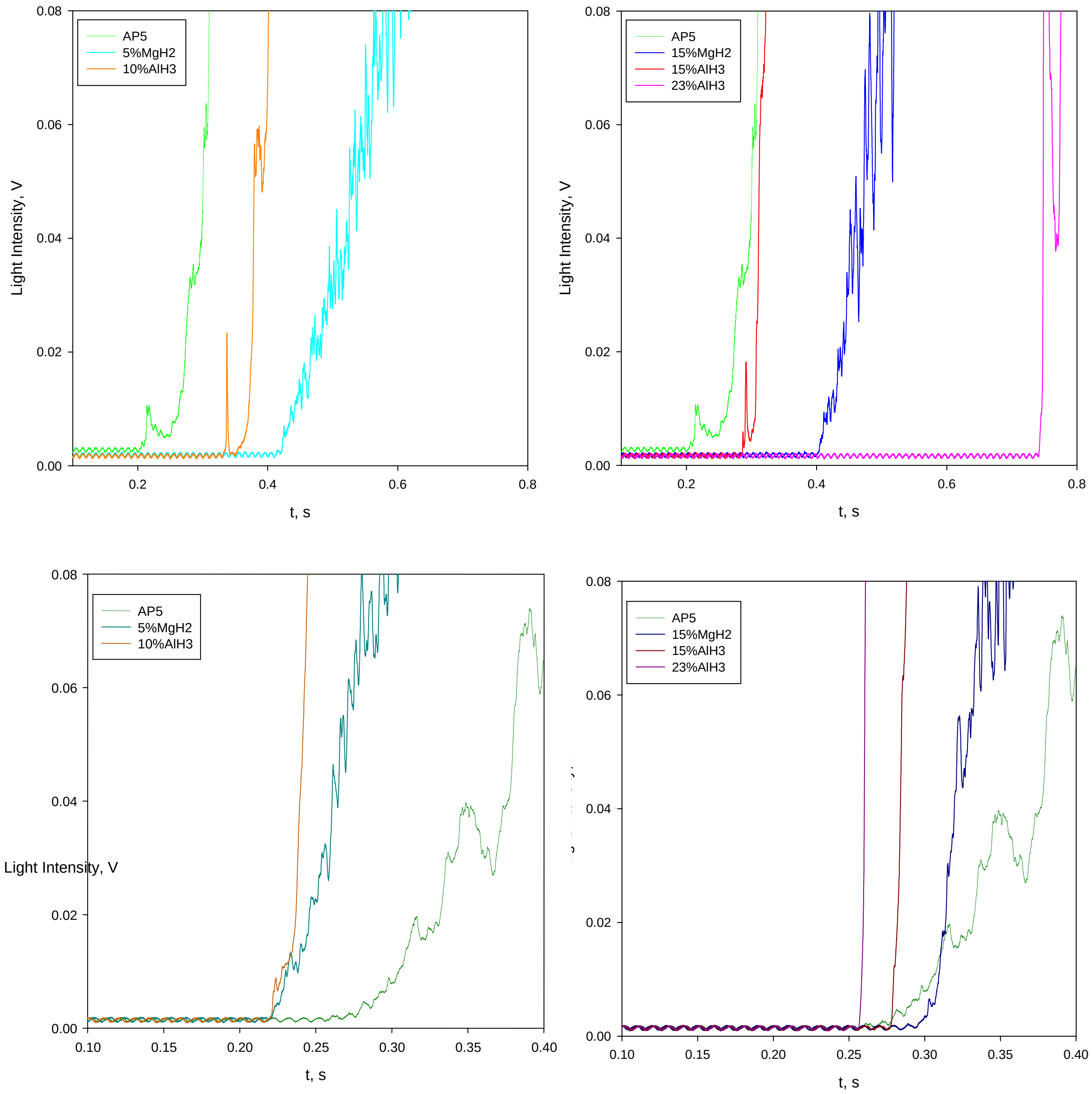

Figure 4: Light emission intensity acquired by the photodiode for low (left) and high (right) metal hydride contents at 0.1 MPa (upper) and 0.5 MPa (lower) nitrogen pressure

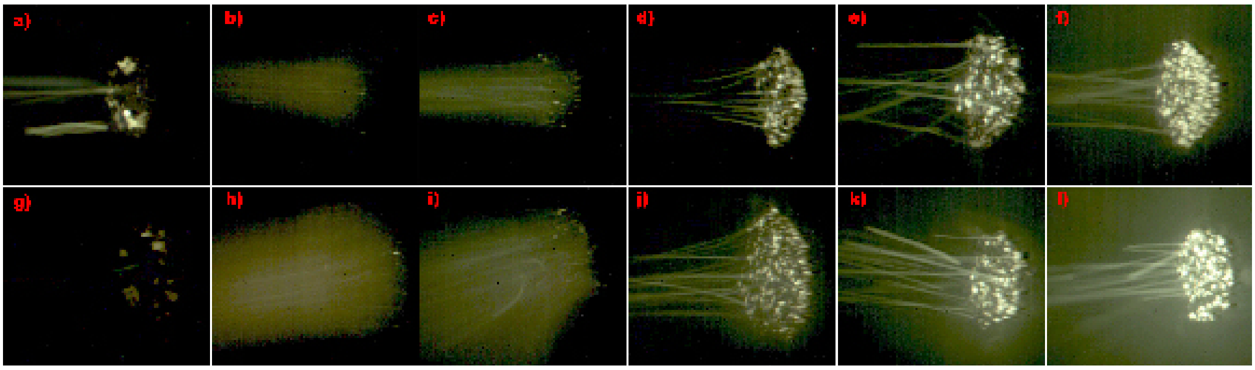

Figure 5: Flame structure captured with a high-speed digital color camera. All tests performed at same luminosity and set-up conditions. Upper row shows 0.1 MPa experiments, while lower row shows 0.5 MPa experiments: a) and g) for reference, b) and h) for 5%MgH_2, c) and i) for 15%MgH_2, d) and j) for 10%AlH_3, e) and k) for 15%AlH_3, f) and l) for 23%AlH_3 formulations

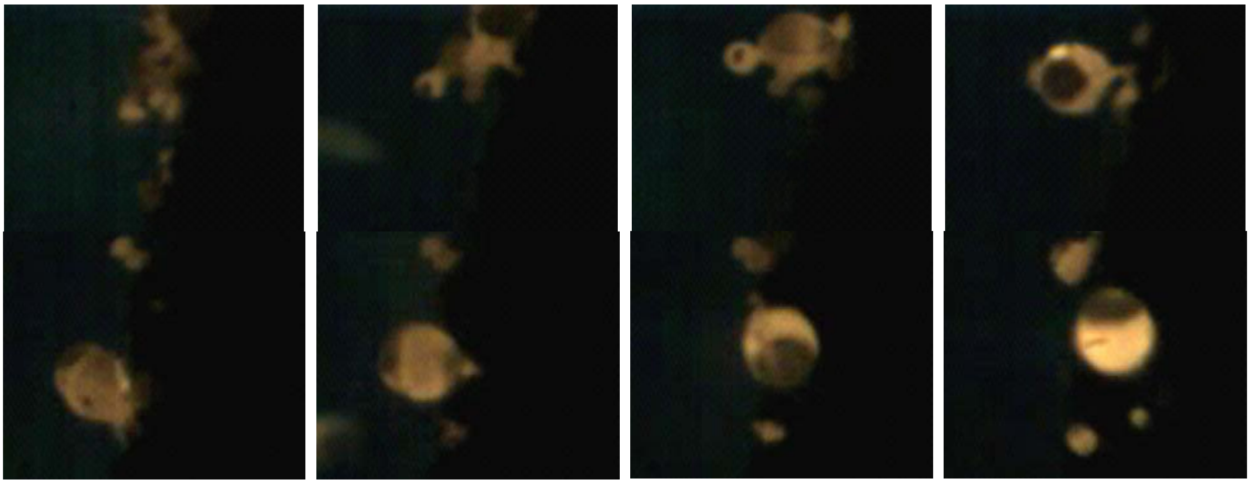

Figure 6: Aggregate/agglomerate mechanism evolution on the burning surface of 5%AlH_3 sample

Conclusions

Ignition is a very complex process, not yet completely understood from a fundamental point of view, but known enough for practical applications. In this work, radiant ignition of metal hydrides based composite solid propellants was investigated. Increasing percentage of aluminum hydrides and magnesium hydrides formulations were ignited with a CO_2 laser in nitrogen atmosphere at different pressure levels. Ignition delay results were found in substantial agreement with standard aluminized propellants with inert binders. Low percentage metal hydrides samples demonstrate a reduced ignition delay compared to AP-HTPB non aluminized propellants, while high percentage metal hydrides samples show ignition boundaries closer to the reference AP-HTPB-Al metallized formulation, although higher pressure level during tests increases the “hydrogen effect” reducing ignition delay up to 63% with respect to standard formulations. Digital, color, high-speed camera movies show different flame structure for aluminum and magnesium hydrides probably due to their different dehydrogenation temperatures, as pointed out by the light emissions recorded by a visible light photodiode.

Aluminum hydrides in solid propellant demonstrated to improve ballistic performance [1]. Both metal hydrides based formulations tested in this study revealed quicker ignition mechanism decreasing the ignition delay up to 63% with respect to conventional AP-HTPB-Al propellants.

Although aluminum hydrides are not still industrially produced, magnesium hydrides is widely used in industry and so available at affordable prices. However, MgH_2 does not guarantee the same performance as aluminum hydrides do. Combustion mechanisms and combustion efficiency investigations should be carried on for all formulations to evaluate their potential usage in low cost and green propellants competitive with the currently used formulations.

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