Reduced Agglomeration in Solid Propellants Containing Porous Aluminum

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Abstract

The use of porous aluminum in solid propellants has been studied. Burning strands were photographed in high speed camera, and combustion products were analyzed in a laser particle analyzer. Experiments show that porous aluminum particles produce smaller agglomerates than regular aluminum over a wide pressure range. The agglomerate diameter ejected from the porous aluminum reaches approximately 60% of the one originating from regular aluminum, corresponding to a dramatic volume decrease of around 65%. It is assumed that the high specific area of the porous aluminum results in faster particle ignition, leading to reduction of the agglomeration phenomena and to ejection of smaller aluminum agglomerates.

1. Introduction

Aluminum is added is solid propellants to increase their energetic performance. However, the tendency of aluminum particles to form large agglomerates implies drawbacks which are more severe for larger agglomerates: two-phase flow losses, incomplete combustion, and slag accumulation inside the motor. The latter phenomenon is particularly pronounced in motors with a submerged nozzle (e.g., in space motors such as the space-shuttle boosters). Slag accumulation is undesirable – it leaves a parasite mass inside the motor, and the hot molten material may damage the insulation. Decrease of the agglomeration phenomena should reduce some of the abovementioned disadvantages and lead to better, more efficient propellants and motors.

Combustion of aluminized solid propellants, including the agglomeration phenomena, has been widely studied over the years. Crump et al. [1] and Gany et al. [2] used high speed photography to study agglomeration phenomena in metalized solid propellants. Price [3] presented an insightful review of metalized propellant combustion, where he also suggests an expression for aluminum particle burning time inside a motor. Boraas [4] and Salita [5] focused on slag formation, its effects and modeling approaches.

A comprehensive overview of agglomeration modeling was offered by Beckstead [6]. His work differentiates the various models into two major groups: (a) models emphasizing geometric concepts; and (b) models emphasizing mechanistic concepts. Within the geometric concepts he includes the well-known “pocket model", offered originally by Crump [1, 7] and developed into mathematical models by Beckstead [8] and by Cohen [9], which has also been adopted by many others. Essentially, they assumed a pocket of binder with aluminum and fine AP particles, confined by coarse AP particles arranged within the propellant. The dimensions of this pocket were to determine the agglomerate size, since only aluminum particles originally concentrated within this pocket could merge into a single large agglomerate. The Cohen model [9] also calculates a temperature profile and aluminum particle residence time, to determine whether the aluminum particle is ejected before or after ignition. Gallier [10] has developed a stochastic method, through which he is able to determine a cluster (namely, pocket) volume. He uses statistical tools to deduce the size of the agglomerate, as well as the fraction of aluminum that agglomerates. His calculations show good agreement with experimental data.

In an early work, Gany and Caveny [11] suggested that reduced agglomeration can be achieved by improving the aluminum particle ignition characteristics and shortening the time of ignition. This approach was later elaborated and supported by Yavor and Gany [12] and Yavor et al. [13]. Their research [11-13] has suggested the concept of an agglomeration number, N_{ag}. It was defined as the ratio between t_{ig} - the characteristic ignition time of the aluminum particle; and t_{ac} - the characteristic accumulation time of aluminum particles within the thin mobile/liquid layer situated at the interface between the solid propellant surface and the gas phase ($N_{ag} = t_{ig} / t_{ac}$). It can be deduced, then, that for $N_{ag} < 1$ reduced agglomeration is expected, as opposed to $N_{ag} > 1$ where the layer is packed with aluminum particles prior to ignition and the diameter of the ejected agglomerate is expected to be larger.

Liu [14] conducted experiments on aluminized solid composite propellant combustion, including AP/HTPB-based propellants using high speed photography. His study shows, as Gany and Caveny [11] stated before, that under certain conditions, a decrease in the original aluminum particles diameter can lead to increased agglomeration.
A complicated numerical packing method was developed by Knott et al. [15] and Jackson et al. [16]. Presumably, they simulate the random geometry of a composite propellant, including the AP and aluminum sites. The random packing method is used to determine the separation distances between aluminum particles. A critical separation distance is introduced, below which agglomeration occurs. The model shows reasonable agreement with experimental data, but that may result from the many degrees of freedom it allows. This approach was further elaborated by a 3-D simulation of combustion of aluminized propellant made by Wang et al. [17]. The temperature profile on, below, and above the burning surface was calculated for various conditions, as well as the velocity, ignition time, and ignition height above the burning surface for different sizes of aluminum particles. Aluminum particles were assumed to merge inside the melt layer both vertically and horizontally. The vertical merging is influenced mainly by the particle detachment-from-surface time and the regression rate. The horizontal merging is affected by the detachment-from-surface time as well as by surface tension forces. The results of the study were validated with experimental data.
Babuk [18] has suggested a "skeletal layer" as the agglomeration process starting point. He suggests a partially decomposed carbonaceous binder with aluminum, aluminum oxide, and perhaps some fine AP. Two classes of mixed condensed systems (MCS) were introduced: class "A" agglomerates consisting mainly of Al_2O_3 with "islands" of Al on its surface (also referred to as "matrix"). They ignite at the bottom of the skeletal layer and burn primarily in a heterogeneous regime. It is argued that class "A" agglomerates form mainly below a defined critical pressure. MCS of class "B" has a more clear distinction between aluminum and its oxide, and its ignition occurs at the top of the skeletal layer. The agglomerates resulting from class "B" MCS are generally smaller and occur at pressures higher than the critical pressure.
Rashkovskii [19] developed a statistical model based on probability concepts of aluminum particles colliding and combining in the propellant sub layers, thus creating agglomerates. He later [20] proposed a detailed model based on aerodynamic (drag) and adhesive forces to determine when an agglomerate leaves the burning surface.
Bandera et al. [21] proposed a method for the determination of agglomerate sizes based on a statistical analysis of computer generated propellant surfaces. They propose using a characteristic length l_{ch}, which is similar in concept to this work's characteristic distance D_e, representing the space between two adjacent AP particles. They predict a decrease in l_{ch} with the increase in AP loading, leading to reduced agglomeration. Their characteristic time was defined as $t_{ch} = 2l_{ch}/\dot{r}$, and was found to follow the relation $D_{43} = 2.892 \cdot t_{ch}^{0.997}$, where D_{43} is the average agglomerate diameter taken from experiments.
Several efforts have been made over the years trying to increase performance and reduce aluminum agglomeration in solid rocket motors. It was thought that using nano-scale aluminum particles would lead to better combustion characteristics. Indeed, works [22-24] show a decrease in ignition temperature as well as higher burning rates for solid propellants containing nano-Al, as oppose to those containing micro scale aluminum particles. However, using nano-Al in propellants has some downsides vs. the use of micron-scale aluminum: relatively high oxide content (due to the oxide shell); much higher cost; and difficulties in preparing the propellant resulting from the high viscosity caused by nano-scale powder.
Other methods involved metal coating of the aluminum particles, to improve their ignition characteristics. Rosenband and Gany [25] developed in-house a nickel coating process. They studied the ignition of nickel-coated and regular aluminum powders in air and nitrogen atmospheres. They reported a substantial decrease of ignition temperature and time for nickel-coated aluminum compared to regular aluminum. One of the reasons may be the exothermic reaction between nickel and aluminum. Another reason may be the formation of a eutectic compound of nickel aluminide having relatively low melting temperature, hence causing enhancement of gaseous oxidizer diffusion. They found that nickel-coated aluminum powders exhibit vigorous ignition and combustion at about 1000K, whereas regular aluminum powders do not ignite at temperatures as high as 1500K (the maximum attainable temperature of the test facility). Moreover, heated powders of nickel-coated aluminum formed a lesser number of large molten agglomerates than regular aluminum powders (Rosenband and Gany [26]), indicating a better and more complete combustion process. Their findings were later supported by Shafirovich et al. [27] that heated nickel coated aluminum particles in various atmospheres with laser. They used light emission to determine ignition point, and found a substantial decrease in ignition time due to nickel coating at wide spectra of nickel loadings and surrounding gases. Andrzejak et al. [28, 29] studied the characteristics of nickel-coated and iron-coated single aluminum particle in regular and micro-gravity conditions. They heated coated particles and measured their temperature profiles, identifying the points where vigorous chemical reactions increase sharply the slope of the temperature-vs.-time curve (what they call "ignition temperature"). 2.38 mm particles were heated by laser in Ar or CO_2 atmospheres. The coating was $7.6\mu m$, $47\mu m$, and $147\mu m$ thick, meaning nickel mass fraction of 0.06, 0.29, and 0.58, respectively. A steep temperature rise was noted at 1325ºC for high nickel loadings (0.29 and 0.58), and was not dependent of Ni fraction or inert gas. The research determines that nickel coating lowers ignition

temperature largely because of the melting of $NiAl_3$ at 854ºC, resulting in intermetallic exothermic reactions that promote ignition.

Yavor and Gany [12] and Yavor et al. [13] used nickel-coated aluminum in composite AP-based solid propellants. They compared the size of agglomerates ejected from the surface of burning propellants containing regular and nickel-coated aluminum particles, in variuos propellant compositions and operating pressures. The results reported showed a substantial decrease in agglomerate size when nickel-coated aluminum was used (25-40% reduction in diameter, corresponding to 60-80% decrease in mass).

In this work, porous aluminum was used in order to reduce agglomeration. High porosity particles are generally characterized by a large specific area. The porous aluminum has been prepared by a special process developed in-house (Fig. 1). It possesses specific area of 10-18 m^2/g, similar to that of the highly reactive nano aluminum. Rosenband and Gany [30] have shown that the ignition characteristics and reactivity of porous aluminum powders of different diameters (10, 25μm) are comparable to those of nano-Al. A substantial decrease in ignition temperature was reported as well as shortening in particle ignition time, with respect to regular aluminum powder. It is assumed that the increased specific area of the porous aluminum promotes particle ignition. As a result, using porous aluminum in solid propellants should lead to smaller ejected agglomerates.

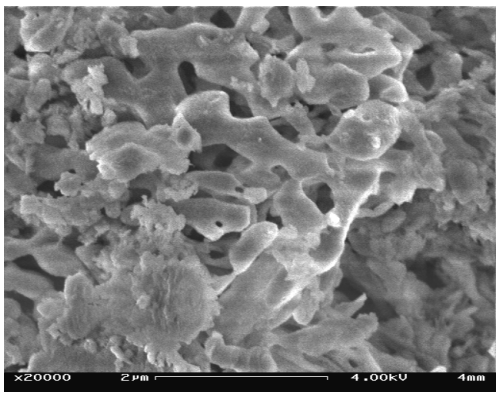


Figure 1: SEM photograph of the surface of a single porous aluminum particle.

2. Experimental Setup

A schematic of the fast photography setup is given in Fig. 2. The pressure chamber includes thick glass windows to view the combustion process of propellant strands. In order to maintain constant pressure inside the chamber, inert gas (nitrogen) is supplied and then discharged, alongside with the combustion products, through a choked nozzle. A high speed video camera was used during the experiments, taking pictures in a frame-rate of up to 5000fps. The burning surface and the zone above it were photographed. Examination and analysis of the pictures were directed to the size and flux of burning aluminum particles/agglomerates ejected from the burning propellant surface.

Experiments were conducted with propellants composing 15% aluminum, 60-65% AP, and 25-20% binder (HTPB or polyester), respectively (mass-wise). The mean diameter of the original aluminum particles used was $25\mu m$, and that of the AP particles was $200\mu m$. Propellants containing regular (as-received) or porous aluminum were compared. The propellants were of the same composition, prepared at the same time and under the same conditions. Experiments have been conducted in both pressurized (up to 34 atm) and atmospheric environments.

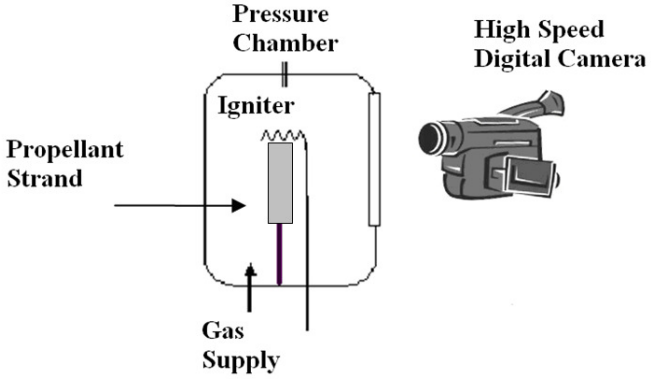
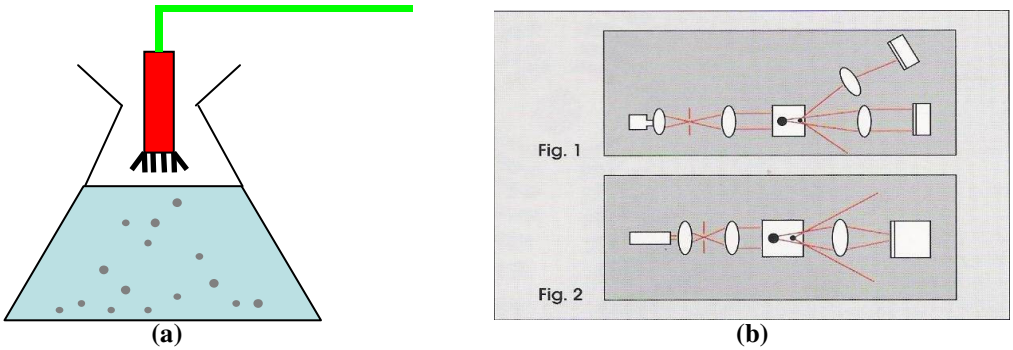


Figure 2: A schematic of the fast photography setup.

In addition, an effort to collect and analyze the combustion products of burning propellants was made. For this purpose, a propellant strand was hung above a glass vessel filled half-way with distilled water (see Fig. 3a). The propellant was then ignited via electrical wire, starting to emit combustion products (including aluminum agglomerates) to the water. The vessel itself was located within a chamber under controlled pressure. Experiments were conducted for propellants containing either regular (as-received) or porous aluminum, at operating pressures ranging from 1 to 25 atmospheres. The condensed-phase products were later poured into a laser particle size analyzer, COULTER LS230, which samples and analyzes particles in the range of 0.04-2000µm (see Fig. 3b).

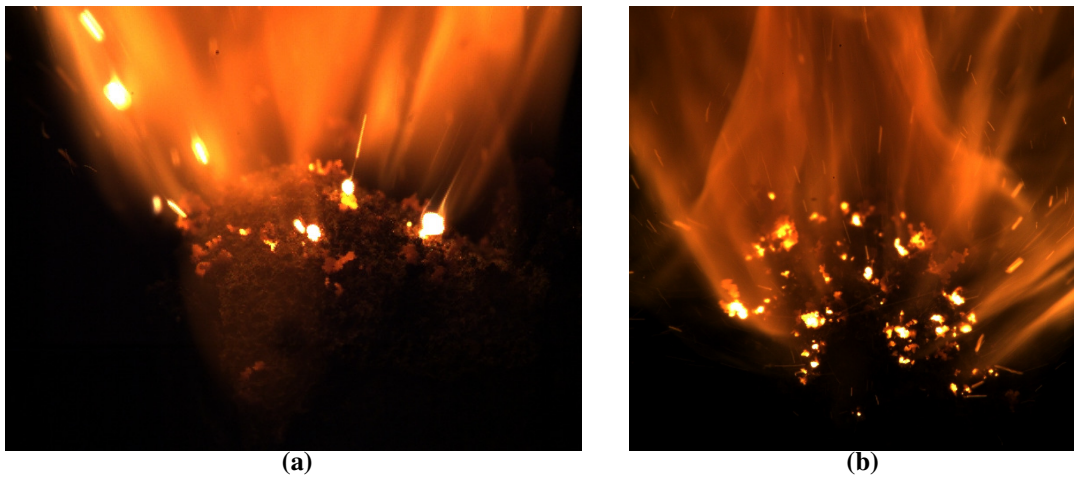


(a) **(b)**

Figure 3: Schematic of (a) burning propellant ejecting combustion products to a glass vessel filled with distilled water; and (b) the COULTER LS230 laser particle size analyzer.

3. Results

The main and most evident finding has been that the use of porous aluminum results in a substantial decrease in agglomeration with respect to the use of regular aluminum.
The combustion of aluminized solid propellant strands is shown in Fig. 4. The propellant strand with porous aluminum particles (Fig. 4b) produces smaller agglomerates than the one with regular aluminum (Fig. 4a). The existence of smaller agglomerates can also be indirectly implied from the higher flux of burning particles/agglomerates ejected from the surface of the propellant containing porous aluminum.



(a) **(b)**

Figure 4: Combustion of polyester-based propellant strands containing 200µm dia. AP and 25µm dia. Al particles at atmospheric pressure. Large agglomerates are observed for the propellant containing regular aluminum (a), whereas the porous Al propellant (b) demonstrates high flux of small particles.

The recorded combustion images were analyzed, mainly by particles count and size measurements, revealing that the initial general prediction of reduction in agglomeration due to porous aluminum was correct.
Typical results obtained for combustion at high pressure (34 atm) are presented in Fig. 5, showing the size distribution of agglomerates ejected from the burning surface for both regular and porous aluminum. Figure 6 presents the cumulative mass percent of the same sampled strands, as observed during combustion. In each and every experiment, a median particle diameter was calculated, for which half of the particles' volume is concentrated in larger particles, and the other half is concentrated in smaller particles. It can be seen that, in the specific test of Fig. 6, the median agglomerate diameter decreased for porous aluminum to 68% of its "original" size (45 vs. 68 micron), resulting in a mass reduction of more than 70%.

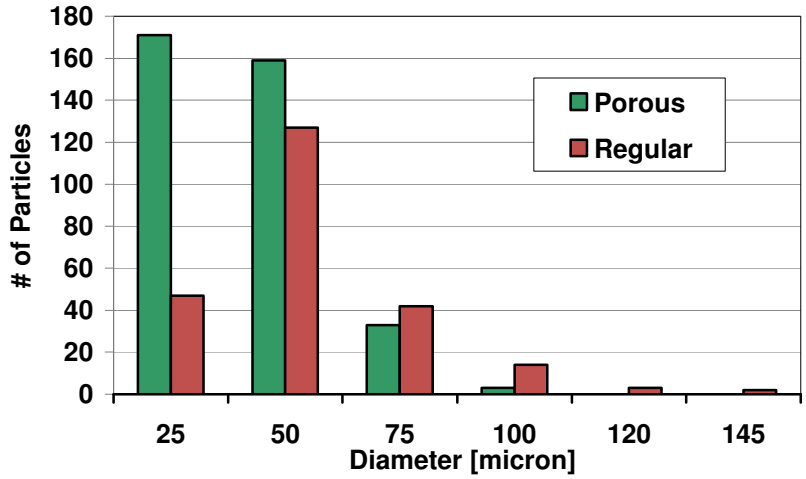


Figure 5: Size distribution of aluminum agglomerates for a 15% Al, 60% AP, 25% HTPB solid propellant strand with a 6x6 mm burning surface, operating at 34 atm.

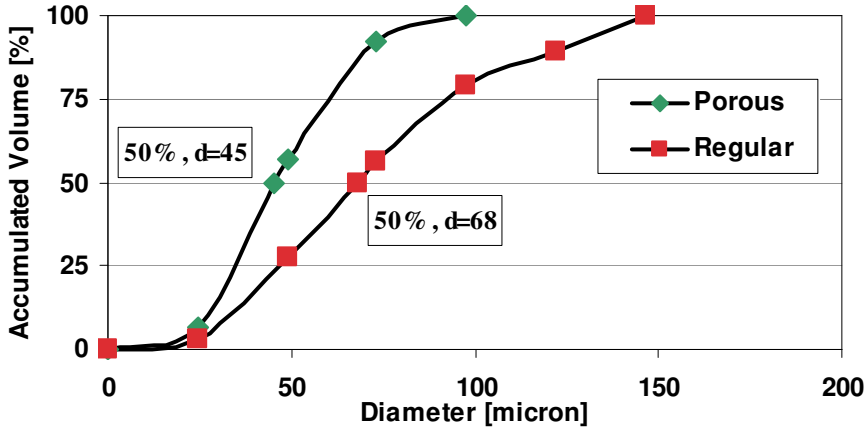


Figure 6: Cumulative mass percentage of ejected aluminum agglomerates in a 60% AP, 15% Al, 25% HTPB solid propellant at 34 atm. The mass-based median diameter is outlined for each case.

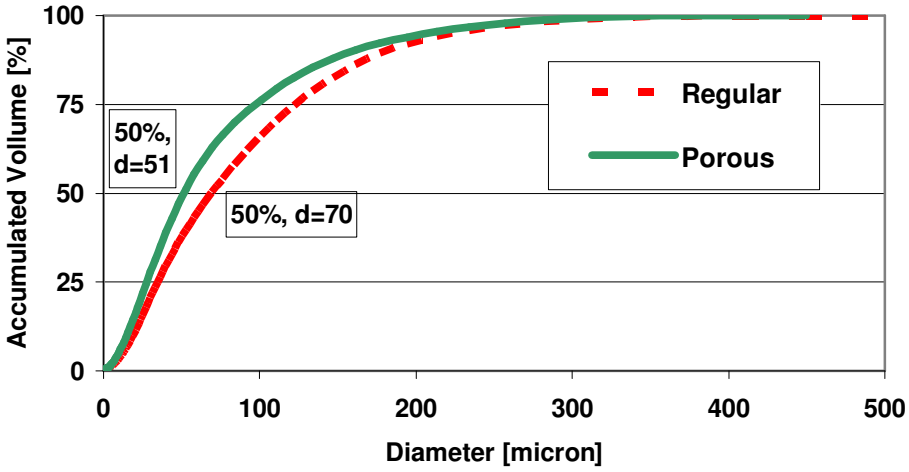


Figure 7: Cumulative mass percentage of ejected aluminum agglomerates in a 60% AP, 15% Al, 25% HTPB solid propellant at 1atm, taken from a laser particle analyzer. The mass-based median diameter is outlined for each case.

Combustion products were examined using the laser particle analyzer. These experiments also revealed a significant decrease in median agglomerate diameter, as suggested in Fig. 7, presenting the results for propellants burning at 1 atm. It can be seen that the median agglomerate diameter decreased for porous aluminum to 73% of its "original" size (51 vs. 70 micron), resulting in a mass reduction of more than 60%.
Figure 8 demonstrates a definite reduction in median agglomerate diameter due to the use of porous aluminum over a range of operating pressures. On average, the diameter of agglomerates resulting from porous aluminum was found to be around 70% of the diameter of agglomerates resulting from regular aluminum. As a result, the “reduced” agglomerate constitutes approximately 35% mass of the “original” one. This reduction is expected to lead to better and more complete combustion of aluminum particles within the solid rocket motor, as well as to reducing slag accumulation.

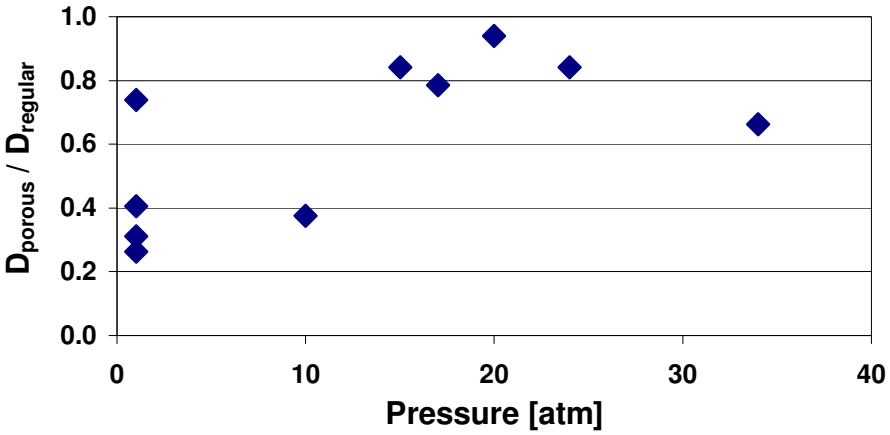


Figure 8: Ejected aluminum agglomerate diameter ratio between porous and regular aluminum particles vs. pressure.

4. Conclusions

The use of porous instead of regular aluminum in solid propellants has been studied. Combustion of propellant strands was photographed and analyzed thoroughly. Experiments show that porous aluminum particles produce smaller agglomerates than regular aluminum over a wide pressure range. Comparison between agglomerates ejected from propellants containing porous and regular aluminum reveals that the median diameter of agglomerates resulting from the porous aluminum reaches around 70% of the one originating from regular as-received aluminum. This reduction in agglomerate diameter corresponds to a substantial volume (and hence, mass) decrease of approximately 65%.
It is assumed that the high specific area of the porous aluminum particles (10-18 m^2/g, similar to that of nano-Al) results in high reactivity, leading to a shorter ignition time, as suggested by Rosenband and Gany [30]. The present results comply with predictions of previous works ([11-13]) that a shorter ignition time limits the accumulation and merging of aluminum particles at the burning surface, leading to reduction of the agglomeration phenomena and to ejection of smaller aluminum agglomerates.

5. Acknowledgements

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