Micro and Nano Scale Phenomena of Aluminum Agglomeration During Solid Propellant Combustion

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Abstract

Combustion of aluminized solid propellants exhibits phenomena associated with accumulation, agglomeration, ignition, and combustion of micro and nano-size aluminum particles. In general, agglomeration is an undesirable phenomenon, as it turns small particles into relatively large agglomerates, each containing many original particles, resulting in long combustion times which may lead to incomplete reaction, reduced jet momentum, and enhanced slag formation which adds parasite mass and may damage the motor insulation. This article presents a physical mechanism explaining the agglomeration process, revealing that small particles tend to agglomerate more than large particles. In addition, it suggests ways to reduce agglomeration of the aluminum particles via nano-coatings generating reactive heating and promoting ignition.

1. Introduction

Aluminum particles are commonly added to solid propellants (up to about 20% mass fraction) to increase their energy and energy density. However, during the propellant combustion, aluminum particles tend to form relatively large agglomerates which are ejected from the propellant surface into the hot gas flow field. This situation may result in undesirable phenomena such as incomplete combustion, two-phase flow losses, and slag accumulation, particularly in motors having a submerged nozzle (e.g., in space motors such as the Space-Shuttle boosters). Besides demonstrating only partial oxidation which decreases the actual propellant energy, the existence of slag reduces the overall jet momentum, adds parasite mass, and may damage the motor insulation.

The objective of this research is to present a physical mechanism explaining the aluminum particle agglomeration process during the combustion of solid propellants and to show its dependence on particle size and operating parameters. In addition, it suggests ways to reduce agglomeration of the aluminum particles via nano-coatings generating reactive heating and promoting ignition.

Numerous studies have been conducted to characterize the combustion of aluminized solid propellants and agglomeration phenomena. A brief review will follow: Crump et al. [1] and Gany et al. [2] used high speed photography to study agglomeration phenomena in metallized solid propellants. Price [3] presented a thorough review on metallized propellant combustion, suggesting an expression for aluminum particle burning time inside a rocket motor. Beckstead [4] offered a model of aluminum particle combustion. It is a 2-D, unsteady state, evaporation-diffusion-kinetics controlled numerical model. It refers to various factors: heat transfer, chemical reactions, diffusion of reactants and products, as well as particle and flame zone characteristics, and solves the conservation equations. When referring to combustion of aluminized propellants, the model assumes ignition on or very close to the burning surface, as the present work suggests. Boraas [5] and Salita [6] focused on slag formation and its effect, presenting different modeling approaches.

A comprehensive overview of agglomeration modeling was offered by Beckstead [7]. His work differentiates the various models into two major groups: (a) models emphasizing mechanistic concepts; and (b) models emphasizing geometric concepts. One of the prominent researches using the mechanistic approach is that of Gany and Caveny [8], which also serves as the basis of the present
work. In their model they assumed that accumulation of aluminum particles takes place within a thin mobile (melt) layer at the propellant burning surface prior to ignition and ejection into the hot gas stream, where the ignition time is often associated with melting and merging of adjacent particles, determining the size of the ejected agglomerate. Hence, an agglomeration number expressing the ratio between ignition and accumulation times indicates whether prominent agglomeration will occur (in case of agglomeration number larger than unity) or substantially reduced agglomeration will take place in the opposite case. Experiments done with homogeneous aluminized solid propellant combustion verified the concept of an “agglomeration limit”, showing that particles smaller than approximately the thickness of the mobile layer are prone to substantial agglomeration, whereas larger particles reveal reduced agglomeration. Based on their model they suggested that reduced agglomeration can be achieved by improving the aluminum particle ignition characteristics and shortening the ignition time. Liu [9] followed the theoretical approach of Gany and Caveny [8], supporting their model by conducting experiments using high-speed-photography of aluminized solid composite propellant combustion, including AP/HTPB-based propellants.

Within the geometric concepts Beckstead includes the well-known “pocket model”, offered originally by Crump et al. [1] and developed into mathematical models by Beckstead [10] and by Cohen [11], and has also been adopted by many others. This model can particularly be applied to composite propellants. Essentially, a pocket of binder with aluminum and possibly fine AP particles, confined by coarse AP particles, has been assumed. The dimensions of this pocket have been assumed to determine the agglomerate size, since only aluminum particles originally concentrated within this pocket can merge to form large single agglomerate. The model also shows calculations of temperature profile and aluminum particle residence time, and concludes whether the aluminum particle is ejected before or after ignition.

A complicated numerical packing method was developed by Knott et al. [12] and Jackson et al. [13]. Presumably, they simulate the random geometry of a composite propellant, including the AP and aluminum sites. The random packing method is used to determine separation distances between aluminum particles. A critical separation distance is introduced, below which agglomeration occurs. The model shows good 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. [14]. Temperature field at the burning surface and its vicinity was shown for various conditions, as well as the velocity, ignition time and ignition height of different 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.

The present work analyzes the combustion of aluminized solid propellants experimentally as well as theoretically, particularly investigating the aluminum agglomeration phenomena and its potential reduction. The use of nano-aluminum and nickel-coated aluminum particles for improving combustion and reducing agglomeration is specifically addressed.

2. Nano aluminum

Nano-aluminum particles as an additive to solid propellants have been the focus of many investigations since the 1990’s (see, e.g., Dokhan et al. [15], Munch et al. [16], Simonenko and Zarko [17], Galfetti et al. [18], De Luca et al. [19], Galfetti et al. [20]) because of their special properties. One should particularly note the very large specific surface compared to micrometric particles (approximately 15 vs. 0.1 m²/g, respectively), which presumably modifies the combustion characteristics of the propellant. It is important to note, however, that processing and preparation of the propellant mix becomes difficult for nano-aluminum content exceeding 6–8% due to the increased viscosity. Hence, only partial replacement of regular, micrometer-range aluminum may be done in practical applications. In addition, if no special measures are applied, the natural oxidation of nano-aluminum particles may occupy as high as 15–20% of the particle mass, reducing the energetic potential substantially.

The main result related to combustion of nano-aluminized propellants, is the increase in burning rate. It is apparently due to the higher heat feedback resulting from the extensive combustion of the nano particles close to the surface. It has been found that decreasing the aluminum particle size from a micrometric range to a nanometric range may double the propellant burning rate, while having only a little effect on the burning rate pressure exponent. Galfetti et al. [20] measured an average burning rate of 6.92 mm/s at 70 bar (7 MPa) for a composite propellant containing 30 μm aluminum.
particles, and 12.14 mm/s when the aluminum was replaced by a 150 nm size particles. Dokhan et al. [15] demonstrated even larger relative change when replacing 30 μm aluminum particles by 100 nm particles.

Another finding is that nano-aluminum particles ignite at a much lower temperature than regular (micrometric range) particles. It is typically observed that regular aluminum particles may ignite only at high temperatures at the range of 1700–2300 K [4], [14], depending on the ignition environment, close to the melting point of the natural protective oxide layer covering the particles (upon melting the oxide layer shrinks, exposing the aluminum core to fast interaction with the surrounding oxidizing atmosphere). Nano-aluminum particles, on the other hand, reveal ignition way below 1000 °C. Ignition temperature of 526 °C (below aluminum melting point, 660 °C) for 40 nm particles, increasing to 742 °C for 1.1 μm particles was reported in Ref. [20]. According to the model developed by Gany and Caveny [8], such low ignition temperatures (and correspondingly, short ignition times) should result in reduced agglomeration, as has also been observed [19].

3. Nickel-coated aluminum: preparation and ignition tests

Production and combustion characteristics of nickel-coated aluminum particles have been studied at the Technion for more than a decade, developing an original process for the nickel coating of aluminum particles (Rosenband and Gany [21]). Typically, the amount of nickel comprises 5% of the overall particle mass. The nickel forms a thin layer appearing as numerous humps, about 100 nm size, on the particle surfaces (Fig. 1), after Rosenband and Gany [21] and [22]).

Preparing nickel-coated aluminum powders in-house, [21] studied their ignition characteristics in air and nitrogen atmospheres in comparison to those of regular aluminum powders. They reported a substantial decrease of ignition temperature and time for the nickel-coated aluminum when compared to the regular aluminum. Nickel-coated aluminum powders exhibited vigorous ignition and combustion at about 1000 K, whereas regular aluminum powders did not ignite at temperatures as high as 1500 K (the maximum attainable temperature of our test facility). See Fig. 2 [23].

Fig. 1. SEM photographs of regular aluminum particles of 6 μm average size (left) and aluminum particles coated by 5 wt.% of nickel (right) [21], [22].

Fig. 2. Aluminum powders electrically heated on a metal tape in air: As-received aluminum (left) fails to ignite at temperatures as high as 1500 K, whereas nickel-coated aluminum (right) experiences vigorous ignition at about 1000 K (Rosenband and Gany [23]).
Similar results were obtained by Shafrivich et al. [24], using laser ignition of levitated nickel-coated aluminum particles, by Andrzejak et al. [25], [26], who studied the ignition of nickel-coated and iron-coated single aluminum particles heated by laser in argon or CO₂ atmospheres under regular and micro-gravity conditions, and by Hahma et al. [27], who conducted a comprehensive investigation on the effect of different atmospheres applying various experimental techniques. One of the reasons for ignition promotion may be the exothermic reaction between nickel and aluminum. This idea is also supported in [25, 26]. Another reason may be the formation of a relatively low melting point eutectic compound of nickel aluminide (e.g., NiAl₃ with a melting temperature of 854 °C), causing enhancement of gaseous oxidizer diffusion through the outer layer to the underlying aluminum.

4. Modeling of agglomeration in aluminized propellants: regular and nickel-coated aluminum

Modeling of agglomeration during combustion of aluminized propellants has applied the approach of Gany and Caveny [8] for homogeneous propellants, modifying it for composite propellants. Based on observations of burning propellant surfaces, Gany and Caveny presumed that the zone within the condensed phase propellant adjacent to the burning surface is characterized by a thin mobile melt layer (a “reaction layer”). This layer is the medium in which aluminum particles accumulate and merge. The regressing burning surface encounters aluminum particles scattered within the melt layer. The surface tension of the regressing burning surface traps the encountered aluminum particles, pulling them and preventing their ejection from the surface. The aluminum particles, moving downwards with the regressing surface, experience drag force due to the relative flow of the liquid medium against them.

The surface tension force retaining the particle within the mobile (liquid) layer can be expressed by:

\[ F_s = \pi d\sigma \sin^2 \alpha \]  

The maximum liquid drag force is:

\[ \text{max} F_D = 3\pi d \mu \dot{r} \]  

where \( F \) denotes force, \( d \) is the individual particle diameter, \( \dot{r} \) is the propellant regression (burning) rate, \( \sigma \) is the mobile (melt) layer surface tension, \( \mu \) is its viscosity, and \( \alpha \) is the particle exposure angle. The balance between these two major forces determines the equilibrium position of the particle (namely, the angle \( \alpha \)) as can be seen in Fig. 3 (after Gany and Caveny [8]):

\[ \sin^2 \alpha = \frac{3\mu \dot{r}}{\sigma} \]  

The retained particles are heated by the heat flux from the hot combustion gas flow through the exposed cap whose relative size is determined by the exposure angle. The particles accumulate within the mobile layer while the burning propellant surface is regressing. This process continues until the mobile layer is fully packed. Additional particles which encounter the mobile layer through the bottom, will then force the accumulation into the gas flow. At this point the top of the accumulation is fully exposed to the heat flux from the gas, and the heating rate is substantially accelerated. Figure 4 presents the packing and accumulation process as described in [8].
Heating of the particles eventually leads to ignition, once the particles attain the ignition temperature. Ignition causes the pile of adjacent particles to melt and merge and form a large molten (burning) agglomerate (typically a spherical droplet). Observations reveal that often the ignition process is violent and abrupt, leading to detachment of the agglomerate from the surface and its ejection into the gas stream. Hence, the degree of agglomeration depends on two competing phenomena: accumulation of the particles and ignition. If substantial accumulation occurs before ignition, the result will be large agglomerates. If on the other hand, only little accumulation takes place before ignition, substantially reduced agglomeration will occur. This leads to a concept of agglomeration number expressing the ratio between ignition and accumulation times:

$$N_{agg} = \frac{t_{ig}}{t_{ac}}$$

(4)

$N_{agg}$ > 1 indicates substantial agglomeration, where $N_{agg}$ < 1 predicts reduced agglomeration. Ignition time $t_{ig}$ is derived from the balance of heat required to reach the ignition temperature (accounting for the sensible enthalpy and the heat of melting) and the heat flux from the gas phase:

$$\rho V \left( C \cdot \Delta T_{ig} + L \right) = \int_{0}^{t_{ig}} q_s A_{ex} \, dt$$

(5)

where the properties relate to the aluminum particle: $\rho$ density, $V$ volume, $C$ specific heat, $\Delta T_{ig}$ temperature difference from initial propellant temperature to ignition temperature, $L$ latent heat of Al melting, $q_s$ heat flux, and $A_{ex}$ exposed cap. Accumulation time $t_{ac}$ is expressed by:

$$t_{ac} = \frac{L_e}{\dot{r} \beta \phi} \left( 1 - \beta \phi \right)$$

(6)

$L_e$ is the thickness of the mobile (liquid) layer, $\dot{r}$ is the propellant regression (burning) rate, $\phi$ is the aluminum volume fraction in the propellant, and $\beta$ is the co-volume coefficient (for cubic array as assumed in this model, it is $6/\pi$).

One can show that the agglomeration number can be expressed as:

$$N_{agg} = \begin{cases} 
\frac{t_{ig} \cdot \dot{r} \beta \phi}{L_e \left( 1 - \beta \phi \right)} & d < L_e \\
\frac{t_{ig} \cdot \dot{r} \beta \phi}{d \left( 1 - \beta \phi \right)} & d > L_e
\end{cases}$$

(7)

For minimum accumulation time $t_{ac, min}$ one assumes one layer of densely packed particles (i.e., a layer of thickness $d$, equal to the particle diameter). Details about the calculation of ignition and accumulation times can be found in [8], and further elaboration is presented by Yavor et al. [28]. Basically, the behavior of those times is dependent on different factors including the fraction of aluminum particles in the propellant, the heat capacity of aluminum, the heat flux to the surface, and the particle size. The ignition temperature is one of the most influential factors on the ignition time. The effect of nickel coating and to a large extent also that of nano-aluminum is through their lower ignition temperature. It is obvious that by reducing the ignition temperature, the ignition time decreases as well, hence decreasing the agglomeration number and reducing agglomeration, as less accumulation takes place before the detachment of the agglomerate from the surface. Figure 5 (after Yavor and Gany [29], who applied the general approach of Gany and Cavney [8]) reveals the predicted behavior of the ignition and accumulation times vs. original particle size for different ignition temperatures. While $t_{ig} = 2000$ K represents the ignition temperature of regular aluminum, the lower temperatures can represent particles with reduced ignition temperature. According to our findings $t_{ig} = 1100$ K may be a good representation for nickel-coated aluminum particles.

The basic model predicts that agglomeration number of unity represents a limit between prominent agglomeration (for $N_{agg} > 1$) and reduced agglomeration (for $N_{agg} < 1$). This limit depends on pressure. The most influential parameter is the mobile (liquid) surface layer thickness which decreases with increasing pressure. In general, prominent agglomeration is predicted for particles smaller than the liquid layer thickness, and reduced agglomeration should occur for larger particles. Nano particles represent a different regime with reduced agglomeration. Figure 6 shows how the reduced ignition temperature of nickel-coated aluminum causes reduction of agglomeration number over a wide range of pressures; hence it is predicted to reduce agglomeration.

The accumulation description as detailed above, following Gany and Cavney’s modeling approach, gives a good physical insight regarding the particle retention and accumulation mechanism at the propellant surface layer and can distinguish between conditions that are prone to produce prominent agglomeration to those that would yield reduced agglomeration. So far it has not taken into account the existence of large ammonium perchlorate (AP) particles which are absent in homogeneous propellant,
but are the main microstructure feature in composite propellants. As stated by Cohen [11] and others, the relatively large AP particles form a microstructure characterized by “pockets” of binder containing aluminum particles. It is assumed here that the AP particles establish discontinuities between adjacent pockets. Hence, the particles accumulation within the mobile layer may not extend laterally beyond this boundary. Such situation together with the thickness of the packed accumulation prior to ignition dominates the actual size of the ejected agglomerates. This concept is elaborated by Yavor et al. [28, 30], who adjusted Gany and Caveny’s model to composite propellants by adding geometrical features to it. The situation is illustrated in Fig. 7.

One can see the position and relative dimensions of the mobile layer consisting of molten binder components containing the aluminum particles (and possibly also fine AP particles) and extended between large (coarse) AP particles. Obviously, when regressing, the width (span) $D_e$ of that layer will change, moving from a maximum between the tops of the AP particles to a minimum for the smallest distance between the particles. It is also dependent on the packing arrangement. The variable distance during regression is illustrated in Fig. 8.

The instantaneous width of the mobile layer is:

$$D_e = \sqrt{D_{e,\text{max}}^2 - \pi\left(D_{AP}/2\right)^2 - h_{AP}^2}$$  \hspace{1cm} (8)

One can now predict the resulting agglomerate size for aluminized composite propellant according to its specific properties and operating conditions:

$$D_{ag} = \sqrt[3]{\frac{6L_e D_e^2}{\pi \cdot \beta} - d^3} \cdot N_{ag} + d^3 \hspace{1cm}; \hspace{0.2cm} d < L_e$$  \hspace{1cm} (9)

$$D_{ag} = \sqrt[3]{\frac{6d \cdot D_e^2}{\pi \cdot \beta} - d^3} \cdot N_{ag} + d^3 \hspace{1cm}; \hspace{0.2cm} d > L_e$$
Figure 9 presents a prediction of average agglomerate diameter vs agglomeration number for a propellant containing 15% of 25 μm aluminum particles, 60% of 200 μm AP particles, and an HTPB binder [30]. One can see that reducing the agglomeration number, the average agglomerate size reduces as well. It demonstrates the significance of nickel coating which reduces the agglomeration number by reducing the particle ignition time (because of the reduced ignition temperature). Theoretically, if the agglomeration number approached zero (namely, zero ignition time), no agglomeration would take place, and the original particles would be ignited and ejected instantly. The figure shows as well that propellant combustion at higher pressures produces smaller agglomerates. This fact is well known from practical applications. The main influencing parameters according to the model are thinner mobile (liquid) layer (due to the higher regression rate) and higher heat flux at higher pressures.

4. Experimental work

A comprehensive experimental work has been conducted to study agglomeration characteristics in general and the effect of nickel coating in particular during the combustion of aluminized composite propellants. The main experimental technique has been a windowed strand burner and high speed photography of the burning surface and ejected agglomerates. Additional supporting data have been received from collecting condensed combustion products and obtaining their size distribution from a particle size analyzer. Parts of the experimental effort have been summarized by Yavor and Gany [29] and Yavor et al. [28], [30].

A schematic view of the test system is presented in Fig. 10. The pressure chamber includes thick glass windows to capture the combustion process of propellant strands. In order to maintain constant pressure inside the chamber, inert gas (nitrogen) is supplied and then discharged, together with the combustion products, through a choked nozzle. A high speed video camera, FASTVIEWER-XL of FastVision (and in a later stage Phantom’s V310), has been used taking pictures in a frame-rate of 1000–3000 fps. The burning surface and the zone above it were photographed. Close examination and analysis were directed to the size and flux of burning aluminum particles/agglomerates ejected from the burning propellant surface.

All propellant compositions contained 15% aluminum (mass-wise). AP and binder made up the rest: Typically 60–65% AP, and 25–20% HTPB, respectively. In some compositions the HTPB was replaced by epoxy, because it produced less smoke. The aluminum particles used were of different diameters (6 μm, 25 μm), and the AP particles 20 μm or 200 μm. Propellants containing regular (as-received) or nickel-coated aluminum were compared. The propellants were of the same composition, prepared at the same time and under the same conditions. Experiments have been conducted under pressure ranging from 1 to 50 atmospheres (0.1 to 5 MPa).

In the experiments two almost identical propellant strands were glued together with epoxy, as shown in Fig. 11. They differed only by their aluminum component, which was either regular (uncoated) or with nickel coating. The glued strands were ignited simultaneously, in order to better observe and notice the effect of the nickel coating.

Figure 12 shows a frame from a movie taken at 1000 pictures per second. A visual inspection of the films reveals that nickel-coated propellants produce smaller agglomerates and a larger flux of ejected agglomerates. Frame by frame analysis of the size of ejected agglomerates from the films yields quantitative data on the size reduction of agglomerates obtained from nickel-coated aluminum (see Yavor et al. [28]).
Figure 13 shows the cumulative mass percent of agglomerates ejected from the burning surface of propellant strands for both regular (uncoated) and nickel-coated aluminum [28].

Figure 11. A view of a double-strand propellant sample (front and upper surfaces are visible). The dark strand (on the right) is the nickel-coated Al propellant.

Figure 12. Combustion of HTPB-based propellant strands containing 60% of 20 μm AP and 15% of 6 μm Al particles. The nickel-coated Al propellant strand is on the right hand side of the picture. Large agglomerates (marked by arrows) are observed for the propellant containing regular (uncoated) aluminum. Higher flux of smaller particles is observed for the propellant containing coated aluminum (after Yavor et al. [28]).

Figure 13. Example of cumulative mass percentage of ejected aluminum agglomerates from a combustion test of a solid propellant containing 15% Al, 60% AP, 25% HTPB at 32 atm. The mass-based median diameter is outlined for each case [28].

Fig. 14. Ejected aluminum agglomerate diameter ratio between coated and uncoated aluminum particles vs. pressure [28].

Fig. 15. Demonstration of the relative size reduction of an average agglomerate resulting from nickel-coated aluminum (on the right) vs. that of regular aluminum.

Summarizing the results obtained with nickel-coated vs. uncoated aluminum, one finds that in the average the aluminized propellants with nickel-coated aluminum produce agglomerates whose diameter is about 70% of those of regular aluminum, meaning agglomerate mass of about one third of the regular aluminum, see Fig. 14 [28]. For better impression one can refer to Fig. 15.

Burning of propellant strands containing nano aluminum (about 100 nanometer size) has been studied as well. High speed photography of the agglomerates ejected from the surface during combustion revealed that nano aluminum produced smaller agglomerates than micron range regular as well as nickel coated particles (Fig. 16). In the average micron range nickel coated aluminum particles produced agglomerates of about 60–70% the size produced by regular aluminum particles, whereas nano particles produced even smaller agglomerates of about 50% of those of regular micron range particles.

Finally, the theoretical model has been compared to the actual test results with respect to prediction of average agglomerate size under different pressures (0.1–5 MPa). The comparison was done for a propellant composed of 15% of 25 μm
5. Conclusions

This research studies theoretically and experimentally the phenomena characterizing the combustion of aluminized propellants. In particular, the effect of nano-aluminum and nickel-coated aluminum on the agglomeration behavior is studied in detail. The nickel coating appears as numerous humps (about 100 nano-meter size) bonded to the particle surface. Nano aluminum is found to increase the propellant burning rate due to higher heat feedback resulting from intense combustion of the particle close to the surface. Processing of propellants with nano-aluminum particles is more difficult due to increased viscosity, practically limiting the amount of nano particles to 6–8%. Nano aluminum particles demonstrate lower ignition temperature and time as well as reduced agglomeration compared to micron-size aluminum (regular or coated). Nevertheless, they imply substantial drawbacks, particularly high cost and loss of energy due to noticeable oxidation reaching as high as 15–20% of the particle mass. Nickel-coated aluminum seems a very good practical solution for improving ignition and reducing agglomeration. It was found experimentally that the diameter of agglomerates resulting from nickel-coated aluminum is about 70% of those of regular aluminum, and the mass is only about one third. It is presumed that the smaller agglomerates should result in less slag accumulation in the motor during firing.

A model based on Gany and Caveny’s [8] approach for aluminum agglomeration and ignition in composite propellants has been developed by introducing the modifications implied from the discontinuities in the microstructure resulting from the coarse AP particles. The model gives good prediction of the ejected agglomerate size over a range of operating pressures.

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References


