

An analysis of the reactivity of nano-sized aluminum powders in solid propellants

Dan Borcea (10678208), dan.borcea@mail.polimi.it

Combustion in Termochemical Propulsion

Politecnico di Milano

Abstract—The main objective of this work is to investigate the relationship between the reactivity of aluminum nano-powder and the ballistic properties of solid propellants containing it. Additionally, it aims to identify the characteristics of the powder that can enhance the performance of these propellants. To achieve this, the study involves analyzing the characterizing parameters of each powder, its thermogravimetric data, and the burning rate as a function of pressure for multiple propellants with different formulations. At the end of this analysis, it was concluded that the diversity in the composition of aluminum powder is the key factor that facilitates the oxidation of aluminum in thermogravimetric traces by reducing the onset time. However, this effect proves to be counterproductive in the combustion of solid propellants when fine ammonium perchlorate particles are included in the formulation.

I. INTRODUCTION

For many decades aluminum powders made of micron sized particles have been exploited to enhance the performance of solid propellant propulsion by increasing the specific impulse and the burning rate. Hence the combustion of aluminum releases a significant amount of enthalpy which can be used to increase the flame temperature of the propellant combustion. The arising need of further enhancing the performance of solid propellants brought to the development and the use of nano sized aluminum particles as a substitution to the micro aluminum powders, thanks to their high specific surface and, as a direct consequence, their remarkable reactivity. By partial substitution with micron sized particles, the nano powders of aluminum can be used to enhance and to tailor the burning rate of solid propellants. The characterization and prediction of the performance boost given by the nano powders, as for the micro powders, is a difficult task due to the multiple factors that play a role, such as the production and storage of the powder, the composition of the solid propellant and the interplay between the complex phenomena which makes the combustion of aluminum at low temperatures possible.

II. GENERAL BACKGROUND THEORY FOR THE OXIDATION OF ALUMINUM

Aluminum rapidly develops a thin layer of amorphous alumina as soon as it is exposed to an oxidative environment. This phenomenon, known as passivation, is generally regarded as a diffusion-controlled process. For oxidation to occur, oxygen transport by aluminum ions is required. As the oxide layer forms, which is both permeable and resistant, the transport becomes increasingly obstructed until the particle stabilizes and is fully isolated from the environment. Typically, the thickness of the alumina layer ranges from 3 to 5 nm and is independent of the particle size (when spherical). Thus, a reduction in particle diameter results in a decrease in aluminum content.

To achieve complete oxidation, aluminum must be heated to temperatures above 2000 °C, which is the melting point of alumina. However, this can be circumvented if a specific event occurs that exposes the aluminum core to the oxidative environment. This event is the transition of alumina to a more thermodynamically stable form, γ -alumina, which occurs at around 500 °C, before the melting temperature of aluminum. This transition happens for both micro and nano-scale aluminum particles. The complete or partial detachment of the oxide layer from the core can occur due to mechanical stress resulting from the density change during the transition from amorphous alumina to γ -alumina. Consequently, the ordered structure of crystalline alumina is denser than the original amorphous form.

For a micro sized particle the exposure of aluminum is followed by a new slow oxidation stage in which the thin alumina layer is being regenerated around the particle. The process is slow because the relatively high volume of the particle implies a lot of heat to be extracted from the energy budget given by the exothermic reaction, in order for the particle to heat up. Therefor it is not possible to ignite the particle at this stage and the oxidation rate is rapidly arrested. For a nano sized aluminum the higher surface to volume ratio leads to a heat balance in which

the heat release due to particle oxidation dominates and the reaction is self sustained, resulting into an aggressive combustion of the particle. Further discussion on the topic will be held in the next chapters.

III. MATERIALS & METHODS

For this study four aluminum powders are considered, each one of them being produced by a different manufacturer. The first sample is a micron sized powder, while the aluminum particles from the other powders are in the nano scale and are supposed to be characterized by very similar average particle size. In TABLE I the parameters which are considered relevant for the understanding of the powder distributions are reported.

Powder	Al content [%]	D43 [μm]	S_{sp} [m^2/g]
Al3	99.5 \pm 0.7	44.2	<0.1
Al01j	85.9 \pm 0.8	0.138	12.6 \pm 0.1
Al18a	84.6 \pm 0.6	0.140	16.9 \pm 0.1
Al19a	79.7 \pm 0.6	0.141	15.8 \pm 0.1

TABLE I: Characterizing parameters for the powders

The active Al content was determined by a volumetric technique exploiting the $\text{Al} + \text{H}_2\text{O}$ reaction in a basic environment (10 wt% NaOH(aq)) [1]. The active aluminum content was determined using a volumetric technique that exploits the $\text{Al} + \text{H}_2\text{O}$ reaction in a basic environment (10 wt% NaOH(aq)) [1]. The D43 value, defined as the ratio of the sum of the particle diameters to the power of four to the sum of the particle diameters to the power of three, was measured using the Malvern Mastersizer 2000, an advanced device based on Mie scattering. The identifiable particles ranged between 20 nm and 2000 μm [2]. The specific surface area (SSA) was determined from N₂ adsorption/desorption isotherms using the BET (Brunauer-Emmett-Teller) method. Furthermore, the samples underwent XRD analysis, which revealed only the presence of aluminum. Therefore, the powders could be considered unaffected by aging.

IV. DISCUSSION ON THE DISTRIBUTION OF THE POWDERS

Analizing the TABLE I, it is possible to note that, while the specific surface of *Al3* is one order of magnitude higher, the three values of the remaining powders are in the same range. *Al18a* proves to be characterized by the highest value of S_{sp} , leading to the hypothesis that *Al18a* is the powder with the finest particles. However, when considering the aluminum content, the three parameters are in contradiction with the specific surfaces,

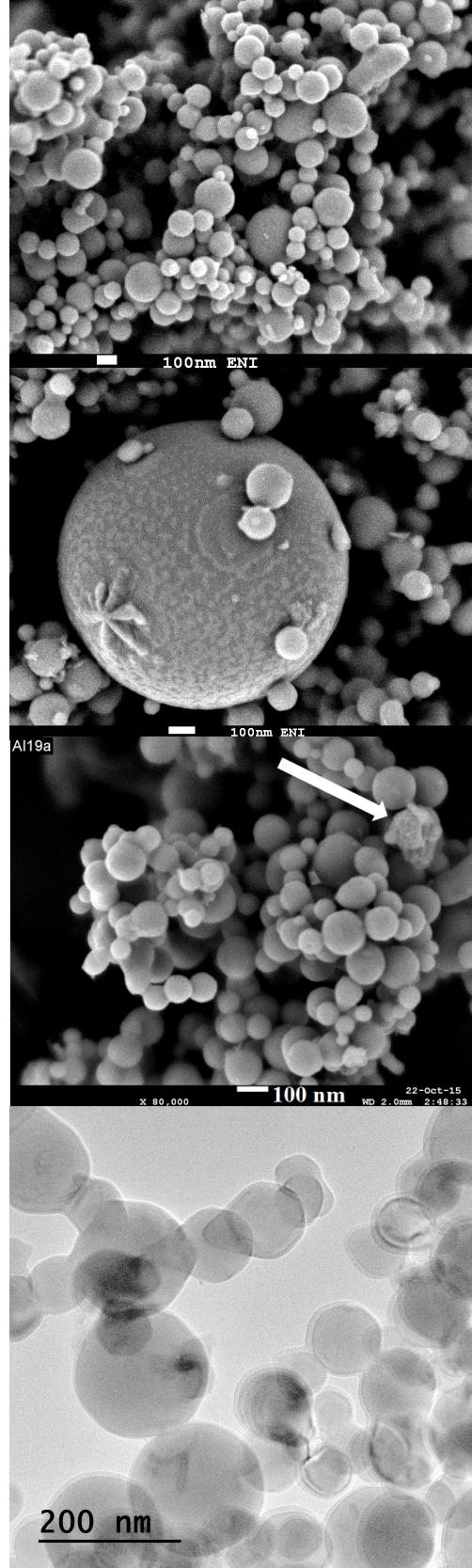


Fig. 1: Starting from the top: SEM measurements for Al01j, Al18a and Al19a nanopowders, TEM measurement for the Al18a powder.

hence the Al mass fraction of *Al01j* is in the same order as *Al18a* and the value characterizing the *Al19a* sample is considerably lower. By considering the D43 parameter, the Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) raffigurations in Fig. 1 it is possible to arrive to some new assessments on the distribution of the powders. The variation of the D43 for the three nano powders is negligible. This average parameter is dependent on the variation of the powder composition, hence it is strongly influenced by the presence of large particles, which appear in the *Al18a* SEM, where a micron sized particle is shown. The enhanced aluminum content in this powder could be directly attributed to the presence of a few very large particles. For the *Al18a* powder to achieve a similar D43 parameter, the small quantity of very large aluminum particles must be balanced by a considerable amount of very small particles. This hypothesis is supported by the SEM image in Fig. 1, where particles with sizes in the order of tens of nanometers are observed, particularly on the surfaces of the largest particles. It is important to note that the Malvern Mastersizer 2000 would still be capable of identifying most of these particles, given the previously mentioned admissible size range. Compared to the recently analyzed SEM, the one corresponding to the *Al01j* powder shows a more uniform particle distribution, the absence of micron-sized particles, and a smaller quantity of particularly small particles.

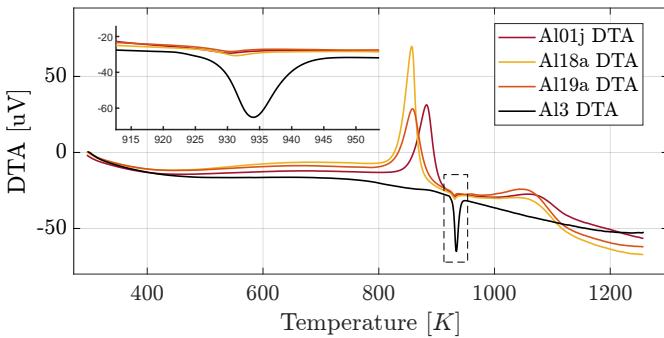


Fig. 2: Differential thermal analysis

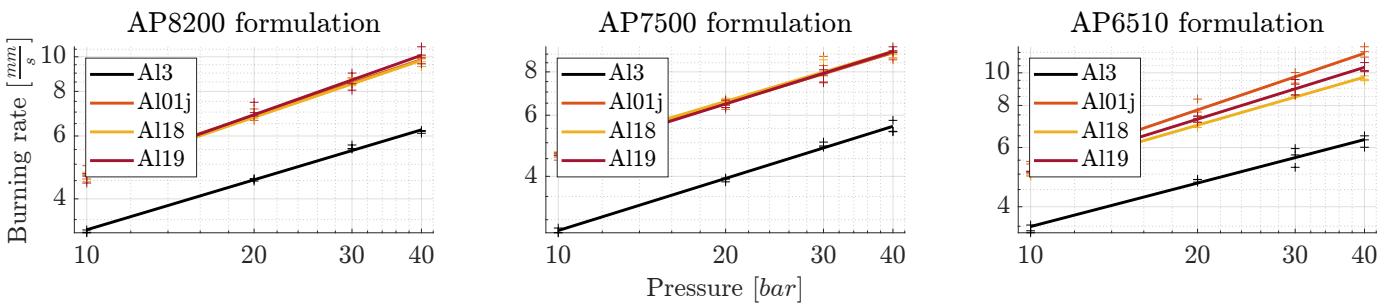


Fig. 3: Ballistic performance for the three propellant formulations and powders

V. DIFFERENTIAL THERMAL ANALYSIS

Thermogravimetry (TG) is a technique used to record the change in mass of a material as a function of temperature or time under a controlled atmosphere. The sample powder is put on a crucible inside a temperature regulated furnace, where temperature is progressively increased by 10 K per minute. It is a qualitative method for identifying the main processes that occur during the slow heating rate of the sample.

In Fig. 2 the differential thermal analysis (DTA) is shown for the four samples. Among the crucible containing the aluminum powder, inside the furnace a reference crucible can also be found and both of them are equipped with a thermocouple. During the slow heating, while the temperature of the reference crucible closely follows the one of the environment, the sample demonstrates a deviation in temperature from the reference crucible. The DTA keeps track of the difference between the two: a positive difference between the two temperatures indicates an exothermic reaction, while a negative one can only be caused by an endothermic process.

Fig. 2 clearly shows an exothermic reaction after 800 K for all the nano sized powders, representing the partial but strong oxidation reaction just after spallation. The exothermic passivation due to the rupture of alumina layer in the micron sized powder cannot be noticed in the chart because the process and enthalpy release are too weak with respect to the negative contribution of the delay due to the higher thermal inertia of the sample crucible.

Shortly after the exothermic peak, at approximately 933 K, an endothermic activity due to the melting of the aluminum core is visible.

VI. BURNING PERFORMANCE OF THE PROPELLANTS

Before going into detail in the thermogravimetric analysis, a short review for the performance of the solid propellants containing the powders will be undertaken, in order to have a wider view of problem when defining the correlating parameter. Each powder was inserted into

three different formulations of propellant that are shown in II.

Propellant	AP coarse [%]	AP fine [%]	Al [%]
AP8200	82	0	4
AP7500	75	0	4
AP6510	65	10	8

TABLE II: Propellant formulations, the remaining percentage is allocated to the HTPB binder fully.

For each powder and for each formulation the burning rate measurements at 10, 20, 30 and 40 bar quasi steady pressures were given. Each single test was performed three times but the Vielle's law fitting of the data was performed once, considering simultaneously all the data (thus no average value was taken for each triplet of tests). In order to save space no table will be plotted for the Vielle's law fitted parameters and the charts in Fig. 3 are exhaustive enough in expressing the performance of the propellants. It is clear that for the first two formulations the burning rate remains almost the same while changing the inserted nano sized powder. By adding finer particles of Ammonium Perchlorate into the propellant the performance is increased for all the propellants but the difference in the effect of each powders becomes also stronger. The propellant containing the *Al01j* powder is the most performing one while the lowest burning rate is given by the *Al18a* powder.

VII. CORRELATION BETWEEN THERMOGRAVIMETRY AND PERFORMANCE

In Fig. 4 the thermogravimetry of each sample powder is shown with the determination of the onset temperature, whose method is the one suggested in [3]. The *Al18a* is the most reactive powder, being characterized by an enhanced conversion of aluminum into oxide (given by the higher mass increase values) and by an anticipated reaction mechanism: the onset time for the first main oxidation and its offset time (especially) are lower with respect to the other two nanosized powders. The reason for this is not strictly known.

A possible theory is that the key feature of the *Al18a* powder enhancing its reactivity is the before mentioned heterogeneity in the particle distribution. The transition of alumina from amorphous to γ should be overcoming at the same temperature (and time) for all particles in each powder but the presence of many and considerably small particles on the surface of the bigger ones creates discontinuities in the formation of the crystalline structure of γ alumina thin layer. The discontinuity, and thus the concentrated stresses during the still occurring transition process, would cause the shell to break in advance, exposing the big aluminum core. Since the particle is considerably big, the rate of oxidation of Al would be leaner, as for micron sized powders, but the presence of the surrounding small and reactive particles gives an additional contribution to the heat balance by radiation. Thus also the increased α conversion would be explained. Since mechanical stresses are stronger if faster temperature variations are applied, the onset

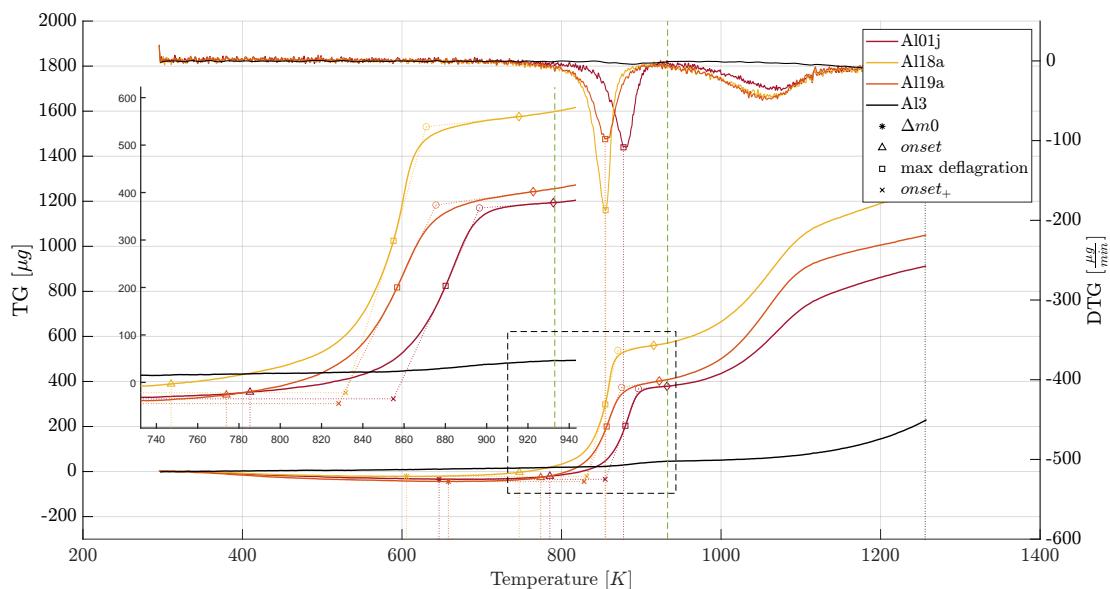


Fig. 4: Traces from the thermogravimetric analysis. On the left axis: the mass variation for the sample. On the right axis: the derivative for the mass variation with respect to time.

temperatures of the three powders would be smaller but the difference between them would probably be larger.

Powder	T_{onset}	$T_{\Delta m_0}$	T_{maxox}	T_{offset}
Al01j	831.8	646.5	896.5	
Al18a	828.3	605.6	854.9	870.7
Al19a	79.7	658.1	0.141	856.6
				875.4

TABLE III: Computed parameters for the reactivity using the tangent method.

From the thermogravimetry a collection of the considered parameters is illustrated in Fig. III. By comparing the propellant burning performance with the reactivity parameters extracted from thermogravimetry of the relative powder there is an interesting inverse correlation between the achieved burning rate and the offset time of the first oxidation. It must be noted before that the difference in the performance for the propellants with different aluminum powders can only be appreciated when fine oxidizer particles are inserted into the pocket with aluminum. This could be an indication that the key feature of the combustion process of aluminum inside solid propellants is related to its oxidation and passivation while still inside the propellant. In the first two formulations, as the burning surface is moving downwards, the Al particles are exposed to the hot environment while still being intact, and no major difference is occurring in the process along the three powders. In the third formulation, aluminum is already surrounded by oxidizer beneath, it is forced to react following a similar life cycle as in thermogravimetric test but faster. While crossing the melting temperature of aluminum the combustion is quenched and if the aluminum is burnt in advance, there is more time for it to passivate before reaching the surface. As a consequence the alumina shell will be regenerated around the core and the particle will need more time to react above the surface. On the contrary, if the first oxidation terminates with higher delay, as for the *Al01j* powder, there won't be enough time for the broken alumina flakes around the core to be sintered to it. After the exposure to the combustion chamber the aluminum aggregates will lose their integrity and will continue on burning while assuming the flake like shapes that is visible in the first and third images of Fig. 5. The image in the center, representing the burning *Al18a* nano powder on the surface, is characterized by more compact spherical aggregates which will require longer time to be burnt and will complete the oxidation farther from the surface. This last consequence can be translated in less heat feedback for the propellant and thus less reactivity.

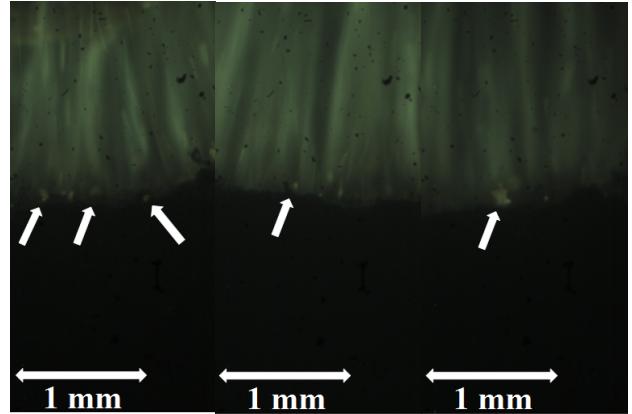


Fig. 5: Starting from the left: burning of Al01j, Al18a and Al19a nano-powders on the surface of fine AP formulation propellant.

VIII. CONCLUSIONS

Two main correlations were found in this study of nano sized powder performance in rocket solid propellants. The first correlation links the heterogeneity in the particle distribution of the powder with its reactivity inside an oxidizing environment. In particular the higher the diversity in the particles size, the more premature the spallation of the oxide layer and the offset of the following oxidation will be.

The second link is between the offset of the first oxidation for the powder and the actual performance of the propellant containing fine AP particles among with the powder itself: the higher the amount of time between the first oxidation and the exposure of the powder to the combustion chamber is, the faster the combustion of the exposed aggregates will be thanks to the uncompleted passivation of aluminum near the cracks of the broken alumina.

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