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Mechanically Activated Al/Mg Powders for Solid Rocket Propellants

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Abstract
The necessity of novel and specialized ingredients for peculiar applications like green solid rocket propellants is boosting the research of novel materials. Several techniques have been introduced in past years to find credible replacements for standard ingredients. However, several problems related to safety, cost, production rate and actual or potential environmental impact hindered the application of these new powders. In this respect, mechanical activation processes represent a viable solution to obtain customized ad hoc ingredients. This work deals with the design, production, and characterization of novel mechanically activated powders for halogen-free solid propellants based on ammonium nitrate. The activated powders, produced by an innovative technique currently under patenting, are characterized "as is" and their effects on solid propellant combustion are evaluated.

1. Introduction

The use of mechanical milling to obtain novel materials with enhanced properties hails from the 1970s, when the first ball milling procedure has been successfully applied to nickel and aluminum powders by Benjamin et al. [1]. In the next 47 years, this technique has been refined, improved and applied for powder production in several fields, from hydrogen generation to rocket propulsion and biomedical engineering [2-4].
Focusing on energetic applications, micron-sized metals are widely used in propulsion, explosives and pyrotechnics. These ingredients are employed in solid rocket motors to increase the gravimetric and volumetric specific impulse, in hybrid rocket engines to enhance the fuel regression rate, in explosives to increase the average pressure peak and impulse, in thermites as reducing agents [5][6]. Most micrometric metals (μM) like Al, Mg, Ti and Fe, feature a relatively low toxicity combined with good stability, safety and availability. These characteristics as well as the lower cost and the higher safety level with respect to nano-sized powders make them very appealing from the industrial point of view. On the other hand, the advantages of micron-sized metals are often associated to peculiar drawbacks, depending on the specific application. In propulsion, for example, micrometric aluminum exhibits a moderate resistance to ignition as well as a low reactivity causing a reduction of rocket performance [14].
Powder characteristics can be successfully modified by processing the virgin materials with proper chemical and mechanical treatments. Activation processes can be classified in three categories according to the selected approach.

- Mechanical activation (MA): in this case, the virgin powder and, if present, the additive, are processed by a mechanical treatment. One of the most used approach is ball milling, in which the powder is grinded through a low or a high-energy mill [7],[8].
- Chemical activation (CA): this process consists in treating chemically the powder, by using different ingredients. Results depend on the activation substance and can vary from a pitting corrosion of particles to a weakening of the external oxide layer passing through a "simple" coating [9],[10].
- Mechano-chemical activation (MCA): in this case, two or more materials are processed together to obtain new species. Generally speaking, a process can be defined mechano-chemical also when a structure change occurs during the process [11].

Among the cited techniques, one of the most promising to enhance performance of micrometric powders is the mechanical activation through high energy ball milling (HEBM). Mechanical activation is a low-cost and versatile

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technique potentially allowing the production of ad-hoc materials. In the propulsion field, for example, it has been used to increase the reactivity of micrometric powders close to nanometric materials keeping, at the same time, a higher safety level. Generally speaking, mechanical activation can be used to produce materials with superior performance with respect to standard ingredients. However, the exact concept of "performance" depends on the final product application which has to be carefully analyzed to determine the treatment target(s) and then the requirements for the new powder (in terms of both safety and properties). This idea is theoretically simple, if not obvious, but its execution is complex due to the amount of parameters which can be varied in a MA processes (e.g. ball to powder mass ratio, milling speed, ball material and size, etc.). Results obtained by several authors have been collected and organized. Despite this excellent work and the new results obtained in this field, it is difficult to forecast the final result of a "general" activation process because a systematic analysis studying the effects of the ball milling parameters on the final product is not yet available. If, from the research point of view, this represent the most limiting factor for MA, the application of HEBM at industrial level is further limited by a low production rate imputable to the maximum amount of powder treatable per each process. This peculiar issue can be solved only reducing the processing time and/or increasing the size of high-energy mills (size and number of the milling vessel, number of ball mills).
In the space propulsion field, HEBM has been already applied for the production of innovative metal fuels to improve the performance of solid rocket motors (SRM) or hybrid rocket engines (HRE). The idea is to increase the reactivity of standard µAl with proper amount of other substances like Mg, B, PTFE, PE, or metal oxides (e.g. Fe2O3, CuO, NiO, etc.). The additive selection and its mass fraction are strongly dependent on the specific final application. In general, metal fuels studied for SRM are characterized by a low amount of additive (usually less than 5%), while ingredients developed for HREs can contain up to 30% of additive [13]. Some examples are reported in [8][13][14][15][16][17]for SRM fuels, and in [14] for HRE ingredients. These choices are related to the specific needs of the two systems. SRMs are characterized by a high burning rate (more than 4 mm/s at 20 bar) and a low specific impulse (up to 300 s), while HREs feature a low regression rate (less than 1 mm/s at 19 bar) and a high specific impulse (more than 350s).

2. Experimental

2.1 Materials

Al have been supplied by AMG Alpoco ltd, UK. As prescribed by the GRAL program, a 15 µm propulsion-grade spherical powder has been used for the manufacturing of Mg-based materials. The powder is characterized by a specific surface area below 1 m^2/g and by an active metal content greater than 98%. Mg was supplied by ALFA AESER. This flake shape powder has a specific surface area below 1 m^2/g. HTPB, AN has been supplied by the partners of the GRAIL project (AVIO and Eurenco Bofors).

2.2 Powder design and production

Standard solid rocket propellants are composed by the 65-70% of ammonium perchlorate (AP, an oxygen rich inorganic salt), by the 15-20% of micrometric aluminum (µAl), and by the 12-15% of a polymeric matrix based on hydroxyl-terminated polybutadiene (HTPB, an inert polymer). This propellant class, belonging to the composite solid propellant family, is costly and environmentally impacting due to the formation of hydrochloric acid. A single launch of Ariane V, for example, is responsible for the emission of more than 90 t of hydrochloric acid. An alternative to AP is the cheap AN, commonly used in agriculture as fertilizer. This salt guarantees a lower environmental impact, but also a reduced burning rate, a limited gravimetric specific impulse a higher pressure deflagration limit [19][20][21]. In past years, this oxidizer was the object of several researches to find a credible low-cost alternative to AP. Difficult burning of AN-based solid propellant was hindered partially replacing Al with a proper amount of Mg [19]. The design of the novel ingredient started from this idea. Unfortunately, the replacement of Al with Mg causes a reduction of the specific impulse as well evidenced by the thermochemical calculation reported in Figure 1. For this reason, activated Al/Mg powders have been designed to enhance the effect of Mg in AN-based solid rocket propellants keeping the amount of Mg as low as possible.

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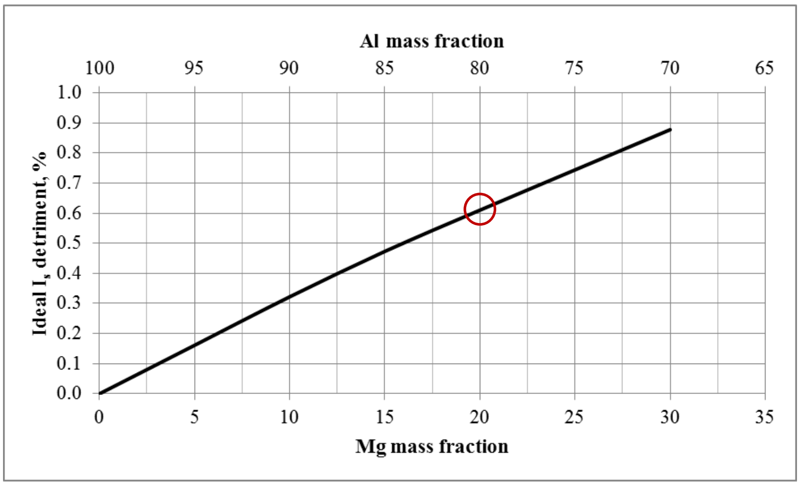

Figure 1. Detriment of the ideal specific impulse caused by the addition of Mg/Al mixtures in HTPB/AN-based SPs under reference conditions. The red circle indicates the design point.

The powder formulation (80% Al and 20% Mg) was chosen looking at the best compromise between final powder reactivity and gravimetric specific impulse preservation.

The increment of metal powder reactivity, main target of the work, has been searched following two well-known strategies in the propulsion field:

- the maximization of the powder specific surface area (particle superficial roughness),
- the strong particle shape variation.

Independently on the selected approach, all the activation procedure guarantees an intimate contact between Mg and Al, further increasing the powder reactivity.

HEBM procedure have been optimized also in terms of eco-compatibility. Treatments were executed in sealed vessels to avoid spillage of both powders and process control agent (distilled acetone). To reduce the environmental impact, the activation process forecasted the recovery of the PCA. About the 90% of acetone used for the activation treatment was recovered at the end of the procedure and reused. All the activation procedures were carried out in Ar for safety reasons. A list of the Al/Mg ingredients produced for this work are reported in Table 1.

Table 1. List of produced materials and activation procedure. For comparison, a powder activate with a standard technique has been added.

Name	Mass of Treated Powder	Milling vessel Volume	Milling vessel material	Sphere Material
Al/Mg (baseline)	-	-	-	-
Act-AlMg_R2	5.0 g	80 ml	AISI 304	AISI 304
Act-AlMg_R3	5.0 g	30 ml	AISI 304	AISI 304
Act-AlMg_PM100*	6.0 g	125 ml	AISI 304	AISI 304

3. Results and discussion

3.1 Powder characterization

Effects of HEBM on the virgin powder particle shape have been studied through a JEOL JSM-7600F Scanning electron microscope (SEM). Figure 2 shows the effects of the different activation procedures on the virgin mixture. The process R2 (under patenting) causes an evident particle flattening. However, the external granule surface remains relatively

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smooth and regular (see Figure 2b). Mg and Al are no longer distinguishable as in subfigure a). The procedure R3 (under patenting) caused not only a “simple” smashing, but also a significant increment of the surface roughness as well as a more consistent particle size reduction (see Figure 2c). The standard technique carried out by a planetary mill RETSCH PM100 induced a lower particle flattening with respect to the novel HEBM treatments, but a superficial roughness similar to the process R3.

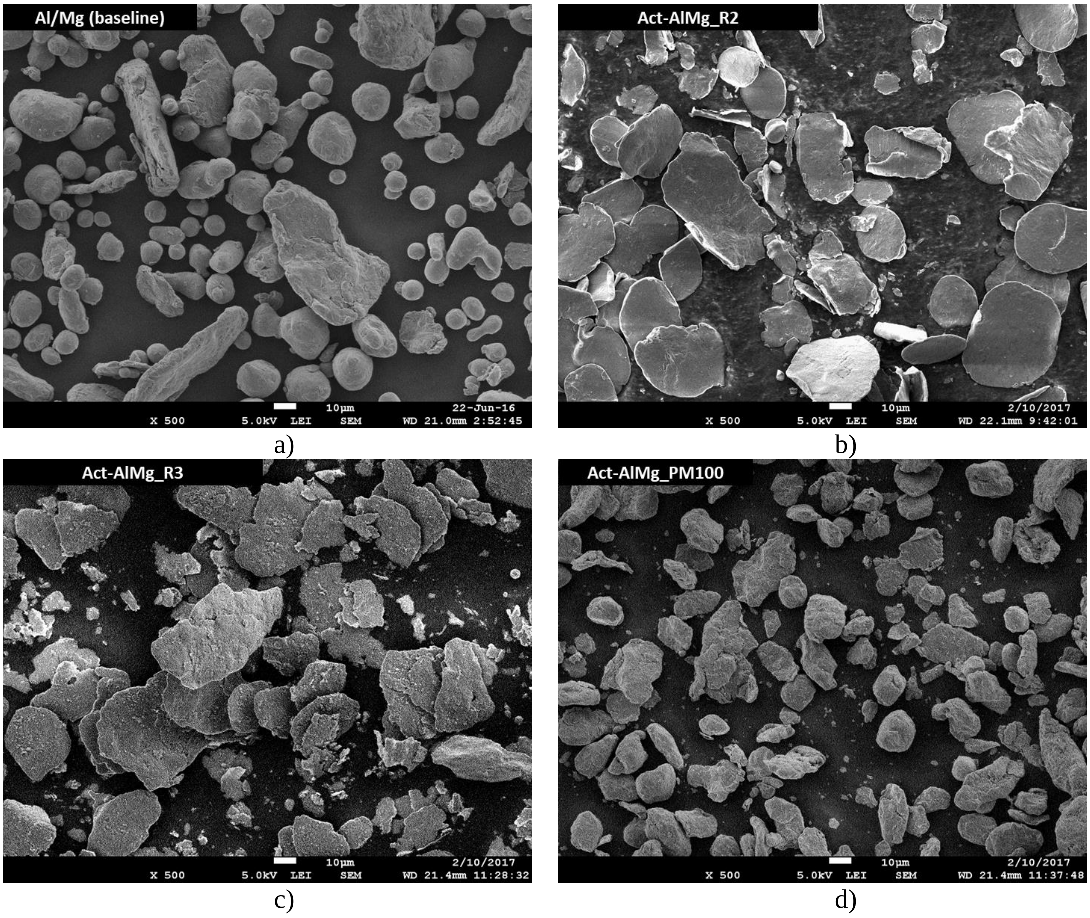

Figure 2. SEM images of activated powders. The virgin mixture and a powder activated through a standard technique (Act-AlMg_PM100) are reported for comparison.

The qualitative observations obtained looking at the SEM images are confirmed by the specific surface area (SSA) analyses reported in Table 2. The powders produced with the standard HEBM technique and with the procedure R2 have a similar SSA. Probably, the strong particle flattening of the sample Act-AlMg_R2 compensate the higher superficial roughness of the ingredient Act-AlMg_PM100. On the contrary, the strong morphological variation of the sample Act-AlMg_R3 leads to the significant SSA value of 26.3 m^2/g.

Table 2. Specific surface area of the tested materials

Name	**SSA, m^2/g**
Al/Mg (baseline)	< 1.0
Act-AlMg_R2	1.66 ± 0.03
Act-AlMg_R3	26.30 ± 0.20
Act-AlMg_PM100	1.19 ± 0.01

Powder reactivity has been evaluated through a SEIKO Exstar 6200 TG-DTA. Tests were performed in air (150 ml/min) from ambient temperature to 1100 °C at 10 °C/min. Results are reported in Table 3 and Figure 3.

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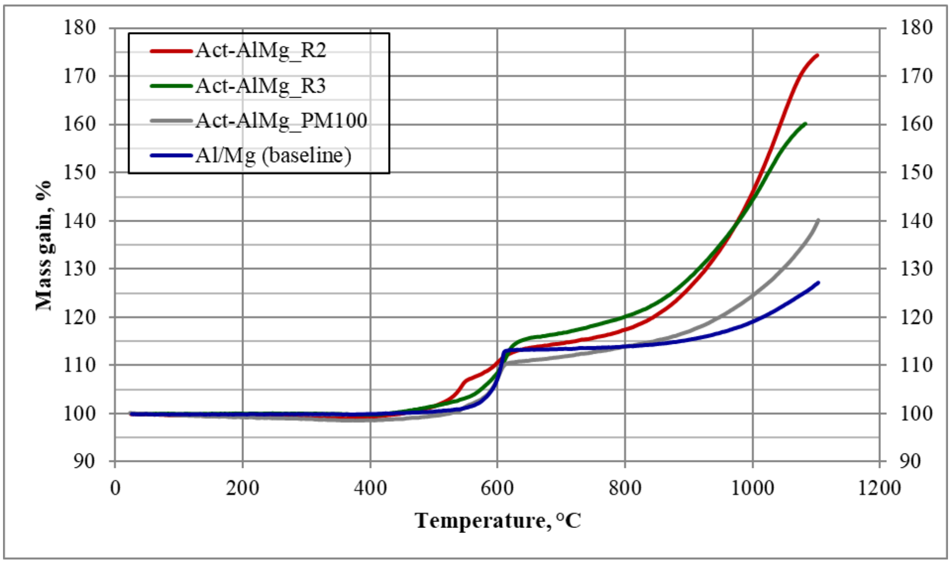

Figure 3. TG traces for the tested samples.

TG traces analysis reveal the capability of HEBM in increasing the reactivity of Al/Mg mixtures. The standard procedure promotes a good mass gain at the end of the test, but also the lowest increment at 700 °C (see Table 3). The cause is probably the reduced Al/Mg intermixing. The highest mass gain at 700 °C has been shown by the powder Act-AlMg_R3 thanks to its high specific surface area. However, at 1080 °C the sample show a lower mass increment with respect to the ingredient Act-AlMg_R2, suggesting a potential depletion of active metal content caused by the peculiar procedure (process R3).

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Table 3. Mass gain at 700 °C and 1080 °C obtained during TG tests of the considered samples.

Label	Mass gain @ 700 °C	Mass gain @1080 °C
Al/Mg (baseline)	13.5 %	27.3 %
Act-AlMg_R2	14.6 %	74.2 %
Act-AlMg_R3	16.7 %	60.1 %
Act-AlMg_PM100*	11.7 %	40.2 %

3.2 Propellant combustion

The novel powders have been characterized as metal fuels in chlorine-free solid propellant formulations. All the propellants were manufactured using a resonant acoustic mixer starting from the same raw material batches. Tested propellant formulations are reported in Table 4.

Table 4. Tested AN-based solid propellant formulations.

Propellant Label	Propellant Formulation					
	Binder	AN	Mg	Al	Act-Metal	Note
P_Al/Mg (baseline)	15 %	65 %	4 %	16 %	-	-
P_Act-AlMg_R2	15 %	65 %	0 %	0 %	20 %	Powder Act-AlMg_R2
P_Act-AlMg_R3	15 %	65 %	0 %	0 %	20 %	Powder Act-AlMg_R3

Experimental ballistic characterization was carried out in a 2l stainless steel horizontal strand burner equipped with two optical accesses for combustion video recording. Tests were executed in nitrogen environment at different pressures kept quasi-steady by a set of electrovalves controlled by an analog regulator. Propellants were cut in 4x4x30 mm samples and laterally inhibited to prevent the propagation of the flame onto the propellant side. Propellant strands have been ignited by a hot wire. A scheme of the experimental set-up is reported in [22].

Data fittings and burning rate values obtained from AN-based propellants are shown in Figure 4. The replacement of the baseline mixture with the activated metal fuel produced by the novel HEBM technique causes a significant increment of the propellant burning rate. Similarly, a progressive enhancement of the pressure sensitivity can be detected. The burning rate enhancement can be imputed partially to the morphology change, and partially to the intermixing between Al and Mg, as testified by the lower r_b of the propellant loading the mixture Act-Al/Mg. The use of activated Al/Mg powders induced also a reduction of the pressure deflagration limit (from 10 bar to less than 5 bar).

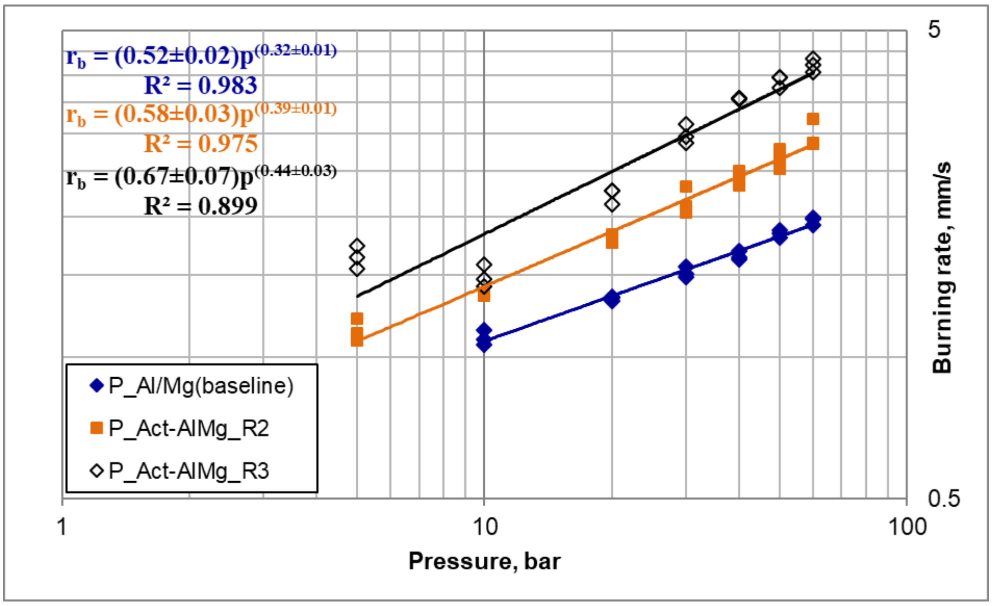

Figure 4. Burning rate of solid rocket propellants loaded with AN and activated Al/Mg powders.

Collection of condensed combustion products has been carried out through a dedicated experimental set-up composed by a 2l stainless steel outer chamber without optical accesses and an internal chamber. The inner chamber, made of brass, aluminium and stainless steel, comprises the quenching pool, the sample holder, and the ignition system. After a proper preparation, cutting and lateral inhibition, the propellant sample (standard dimensions: 4 mm x 4 mm x 30 mm) was positioned on the sample holder and connected to the igniter, a FeCrAl wire heated by Joule effect. Tests were executed in nitrogen environment keeping the pressure quasi-steady through a set of electrovalves controlled by an analog regulator. The quenching liquid selected for this test campaign was tetrachloroethylene. The burning configuration, upside-down, allows a fast and reliable collection of coarse CCPs, while small particles are letting deposit waiting 10 minutes before opening the chamber at the end of the test. Three tests per each pressure have been executed. CCPs were analyzed in terms of particle size distribution by a Malvern Mastersizer 2000 laser granulometer (dispersant: air). Only the formulations P_Al/Mg and P_Act-AlMg_R2 have been tested at 10 bar and 40 bar.

The mass weighted mean diameters of CCPs have been reported in Table 5. Mechanically activated powders feature a good capability in reducing the size of CCPs. Considering the average values, the use of activated aluminium instead of the simple Al/Mg mixture guarantees a CCP size reduction ranging from about 25% at 10 bar up to 45% at 40 bar.

Table 5. CCP mass weighted mean diameter for the tested formulations. Errors have been computed considering a t_student distribution with a confidence level of 95%.

Propellant Label	**CCP D43, μm 10bar**	**CCP D43, μm 40bar**
P_Al/Mg (baseline)	456.8 ± 44.8	257.1 ± 7.6
P_Act-AlMg_R2	345.2 ± 56.2	142.9 ± 7.3

3.3 Discussion

Looking at the results and at the defined targets for the activation procedure, the most interesting (but not definitive) powder is the ingredient Act-AlMg_R2. The propellant combustion analysis revealed a good enhancement of the burning rate for both the powders processed through the novel technique (process R2 and R3), but the ingredient Act-AlMg_R3 shows a non-well-defined behavior, especially at low pressure. Moreover, despite the higher SSA, the preliminary ingredient characterization evidenced a lower final mass gain with respect to the sample Act-AlMg_R2,

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suggesting a potential inferior metal content. Unfortunately, the burning rate guaranteed by the Act-AlMg_R2 is not yet sufficient for a launcher which require a burning rate at 70 bar between 7 mm/s and 15 mm/s [23]. Both the activation procedure, R2 and R3, can give good results, but should be properly modified to center the final objective.

Another major problem is the reduced production rate. LEBM can currently be used at industrial level thanks to the large size of industrial low energy mill (e.g. horizontal machines). The situation is completely different for HEBM processes. In this case, the mill size is relatively small relegating this procedure at lab scale level. The most used high energy mills have 1 to 4 grinding vessels with a maximum volume of 500 ml limiting the amount of treatable powder. At the space propulsion laboratory, 2 different mills are available. One low energy centrifugal mill and one planetary mill. At the moment, the maximum production rate reached is around 30 g per process, but the powder presented in this work can be produced at a rate of 5g/6g per process. Too low for an industrial process.

The new procedure can be easily scaled up. In the near future, it will be possible to increase the production rate up to more than 100 kg of powder per process. Anyway, the reader should notice that the new is complementary to standard techniques and it is not a replacement. This means that the scalability of standard HEBM techniques remains, and will remain for several years, a hot topic.

From the economical point of view, the use of activated materials appears extremely interesting because they are capable to hinder some peculiar problems occurring with green cheap oxidizers. The production cost is higher if compared to standard materials like µAl, however the advantages in terms of cost and environmental impact of the entire system are preponderant.

4. Conclusion

This work deals with the design, production and characterization of Al/Mg activated powders for low-cost green solid rocket propellants. The design strategy for novel activated ingredients adopted at the SPLab has been descried and applied to the specific case. Three different activated materials were produced. Two with an innovative HEBM technique studied at POLIMI and currently under patenting, one using a standard methodology.

All the three activated ingredients and a reference mixture have been characterized in terms of qualitative morphology, specific surface area, purity and behavior at low heating rate. The metal fuels produce through the novel technique were tested also in AN-based solid rocket propellants.

All the activated powders featured a strong morphology variation with respect to the raw material. The exact particle shape was influenced by the peculiar production methodology. The novel HEBM technique proved to be more effective than the standard methodology in increasing both reactivity and specific surface area Al/Mg powders.

Powders activate with the novel technique guarantees a significant enhancement of propellant burning rate as well as an appreciable reduction of CCP size. However, despite the encouraging results, both the two powders produced through the novel technique requires some more improvements in order to be considered for an actual application, although low cost.

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