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Activated aluminum powders for space propulsion

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ABSTRACT

Aluminum powders are commonly used in solid propellants to enhance the performance of space propulsion systems. During combustion, a fraction of the fuel metal particles, which emerge from the bulk, tends to merge into aggregates. These structures eventually leave the combustion surface in the shape of partially molten agglomerates which can reach the size of hundreds of microns. These condensed combustion products partake in nozzle expansion and hinder the delivered specific impulse of the rocket unit. The enhancement of original particle reactivity improves combustion quality and may reduce sensibly agglomerate size and relevant losses. More reactive aluminum fuel can be obtained by activation of micron-sized powders, without resorting to the use of nano-metals. One of the methods consists of a chemical treatment with a processing solution which alters the standard oxide layer at the surface of the particles. Such modifications grant lower ignition temperature and faster propellant burning rates but deplete a fraction of the active metal content, as a result of the chemical reaction.

The present paper compares the features of three batches of aluminum particles which were treated with fluorine-based activating solutions of different concentrations. The batches were supplied in the frame of HISP FP7 European Project. The characterization focused on physical, chemical and thermal properties, looking at the reactivity of the samples and at the alterations introduced by the chemical processing. Finally, activated aluminum batches were tested in lab-scale propellants, monitoring the variation of ballistic properties with respect to a reference formulation.

1. Introduction

Gravimetric and volumetric specific impulse of solid rocket motors can be enhanced by using energetic additives [1–3]. Among the others, aluminum has been adopted in solid space propulsion for decades, in the shape of micrometric metal powders, thanks to its appealing energetic content (30 kJ/g), stability in time, non-toxicity, and relatively low cost. Typical particle sizes range from 5 to 50 μm [4,5].

A fraction of the metal embedded in a propellant tends to aggregate and agglomerate during combustion. Drops of molten aluminum with an oxide cap leave the burning surface [6,7]. These condensed combustion products generate a multiphase flow which expands through the nozzle. Performance losses are the order of 2–5% of the ideal specific impulse, depending on the size and amount of the particulate [8,9]. In this respect, the improvement of metal fuel ignition and combustion is envisaged in order to obtain finer agglomerates, or no agglomeration at all [3,10].

Aluminum particles are covered by a natural oxide layer, as soon as they get in contact with oxygen-containing environments. This passivation shell represents a strong shield against further degradation by the atmospheric oxygen. At the same time, it represents an obstacle to reactivity. Under burning conditions, ignition occurs when the passivating alumina shell fails, enabling fast oxidation of the metal core. The melting temperature of the oxide layer (about 2300 K) is necessary to trigger the combustion, when particle size is in the order of tens of micrometers. Nevertheless, values as low as 1300 K were recorded in the presence of some kinds of active media (namely, combustion products inside rocket core flow) [11]. Ignition temperature is below 900–1000 K, for nanometric powders. Particles take advantage of the sample specific surface and active coating layers, if any [12].

Literature data agree on the fact that the use of nanometric particles in propellants improves ignition and combustion properties, preventing from large agglomerates [13–15]. However, the reduction of particle size introduces some drawbacks. The relative amount of aluminum oxide with respect to the total particle mass can become relevant in the nanometric range, since the thickness of the oxide layer (about 2.5–3 nm) does not scale with particle size [16]. The consequent reduction of the active metal content depresses the available oxidation enthalpy and, in turn, propulsion performance (namely, ideal specific impulse). Moreover, mixing and casting of a propellant containing

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Nomenclature

Acronyms

BET	Brunauer–Emmett–Teller
DTA	differential thermal analysis
ESD	Electro Static Discharge
FCC	face-centered cubic
SEM	scanning electron microscopy
TGA	thermal gravimetric analysis
TMD	theoretical max density
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Greek symbols

α	degree of transformation
Δx	variation of x
ρ	density, g/cm^3

Roman symbols

C_{Al}	active metal fraction
$D_{4,3}$	mass-mean diameter
m	mass, kg
r_b	burning rate, mm/s
p	pressure, bar

Subscripts and superscripts

Id	ideal
In	initial condition
P	propellant
zK	ref. to z Kelvin

nanometric ingredients may represent a technological issue due to high viscosity, reduced pot life, ESD (Electro Static Discharge) and impact hazards as well as cost of the manufactured compound [17].

Specific activation processes can be performed on metal particles to improve ignition and combustion properties, without decreasing the diameter to the sub-micrometric range. Mechanical ball milling, coating with properly chosen metals, or chemical weakening of the external oxide layer represent some examples. Mechanical milling operates a modification of particle morphology by high-energy impact with processing spheres. Synthesis of amorphous powders, structure change, production of metal–ceramics, or inclusions of reactants (metal oxides or fluorides) can be achieved [18–21]. Coating of particles through deposition of metals can improve ignition and combustion properties, such as for magnesium-coated boron [22–24]. The weakening of the oxide shell can be pursued through chemical treatment. A complex fluoride acts as solvent for alumina, lowering the melting point of the protective aluminum oxide layer as well as accelerating the diffusion of gaseous oxidizer towards the metal core [25,26].

The present paper focuses on the effects produced by a chemical activation process. Aluminum powder treated with three different activating solutions of varying concentrations is considered. Physical, chemical, and thermal characterizations, typically applied to nanometric powders, are performed to evaluate reactivity and final quality of the material [13,27]. Comparison with original non-treated micron-sized Al as well as with some representative literature data for nanoaluminum and microaluminum is carried out. Combustion analysis of solid propellant samples containing activated powders is presented.

2. Experimental

Three batches of activated aluminum powders (A-Al01, A-Al02 and A-Al03) have been produced, following a procedure similar to the one described by Hahma [25,28]. The initial aluminum was Valimet H3 powder (batch 07-8002). The producer rated 99.0% of minimum metal content and particle size of 4.5 μm [29]. The activation process was accomplished by a fluorine-based solution, whose concentration was varied to modify the strength of the treatment. The batch A-Al01 was assumed as reference for the processed family. The concentration of the solution was half for A-Al02 and 1.5 times for A-Al03. Powder processing was conducted at FOI (Swedish Defence Research Agency), as part of the HISP (High performance solid propellants for In-Space Propulsion) FP7 project.

The characterization tests of the powders comprised laser granulometry, SEM, XRD, XPS, evaluation of the active metal content, and TGA/DTA scans. Different composite solid rocket propellants were compounded and their ballistic properties were experimentally tested. Moreover, the contraction of ideal performance, following the depletion of metallic aluminum during activation, was monitored by means of thermochemical analysis [30].

2.1. Physical characterization

SEM micrographs, reported in Fig. 1, show a comparison between Valimet H3 and all activated batches. Particles appear mainly spherical. The external surface is smooth for the original powders and rough for the processed ones. The activated particles also feature some irregular deposits, not present in the original material, whose size seems to follow the concentration of the activating solution. Namely, the spots covering the A-Al03 surface reach the size of about 100 nm, whereas smaller dimensions are observed in other cases. A precise estimation is difficult to supply.

Particle size was measured by means of a Malvern Mastersizer 2000 using air dispersion with a Scirocco dry unit. Mass-mean diameter $D_{4,3}$, span of the distribution, and evaluation for the specific surface, derived from geometric considerations, are reported in Table 1. Valimet H3 and activated powders do not demonstrate appreciable differences. All particles have a comparable mass-weighted diameter ranging between 5.1 and 5.5 μm and similar distribution shape and relevant span. For all activated powders, mean particle diameter grows a few hundreds of nanometers. Representative distribution plots are reported in Fig. 2 for A-Al01 and H3. Reduction of the particles finer than 1 μm diameter, presumably lost during the chemical process, is observed.

A more representative evaluation of the powder specific surface is accomplished using the BET technique [33]. The estimation is based on the quantity of adsorbed inert gas on the surface of a sample. The result depends on both geometric aspect of the particles and on the peculiarities of the surface (namely, roughness) [35]. According to Barret, particle characterization is accomplished when size, shape and finish are addressed [36]. Bouwman and co-authors stress on the fact that surface roughness and shape are difficult to define since their distinction derives, in general, from considerations on characteristic dimensions which, in turn, depend on the observation scale [37]. In this respect, the specific surface measurement using the BET technique is a condensed and comprehensive value, which includes all contributions. This kind of analysis has been adopted in the past to characterize fine and ultra-fine metal powders, also for energetic purposes. The measurement was considered a reliable index of reactivity [10,34].

The resulting trend among the tested batches is correlated with the concentration of the activating solution. The specific surface from BET analysis is incremented by the activation process. The reference A-Al01 doubles the specific surface, if compared to the original H3 supply. A-Al02 features the lowest BET improvement while A-Al03 has the highest value, respectively less-than-double and almost three times the value of H3 batch. Laser granulometry assessed that the mean