Nano-composites for rocket solid propellants

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Abstract

Aim of this work is the study of different components (binder and aluminum powders) of solid propellants used for rocket propulsion to improve ballistic performance. New propellant formulations have been tested and characterised. Combustion residues were collected by a proprietary method and analyzed both from the morphological and chemical point of view.
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1. Introduction

Rocket solid propellants for space applications are composite materials, constituted by the major part of an oxidation agent (an inorganic salt as ammonium perchlorate AP); a metallic filler being a good fuel (aluminum powder) and an organic binder (typically a polymeric matrix as hydroxyl-terminated polybutadiene HTPB) [1,2]. For conventional-sized Al (of the order of 10 μm), the Al powder in AP-HTPB propellant is initially clustered, due to packing among large AP particles. The HTPB/AP/Al matrix is very fuel-rich. When a submerged Al particle is exposed to the burning surface, it is usually stuck in a layer of semi-liquid binder. It is experimentally observed that Al tends to reside on the surface for a relatively long time, because of its very high evaporation temperature (2194 K), much higher than that of the binder (HTPB) and of the oxidant (AP) [3]. This leads to concentration and agglomeration of Al-particles at the burning surface. Al is extremely reactive but particles usually have a refractory coating (Al_2O_3) that limits the contact between Al and the surrounding oxidant molecules, until the temperature degrades the oxide coating otherwise limiting the oxidation.

Combustion of solid rocket propellants results in formation of condensed combustion products which have an important influence on rocket motor performance [4]. The detailed knowledge of the powder dispersion characteristics, of the agglomeration mechanism, of the residual size distribution and burning time, are essential points for motor design and to improve rocket performance.

The particles and agglomerates formed by condensation of the gas-phase reaction products have a size of the order of about 1 μm and they account for about 80–90% of the oxide formed by combustion. These particles are effective in damping high frequency oscillations, typically above 4000 Hz. Residue agglomerates mainly consist of aluminum oxide, aluminum and carbon. They are formed by an oxide skin that surrounds the original Al core. These particles may reach hundreds and even thousands micrometers; and they are effective at damping low to mid frequency oscillations. For example, the optimum particle size for damping 500 Hz oscillations is 10–30 μm. The phenomenon of metal agglomeration unfortunately limits the actual performance of metallized propellants but, at the same time, is a powerful mean to control combustion instabilities occurring in the rocket motor.

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Aim of this paper is the study of the Al size and of the binder nature influence on the burning rates and residue oxide products of propellants. High speed video-camera recording, burning rate measurements, and residue oxide analysis performed by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and scanning electron microscopy (SEM), have been obtained for several propellant formulations, designed and manufactured at the Solid Propulsion Laboratory of Politecnico di Milano.

2. Propellant formulations

The formulations of SP Lab propellants investigated in this paper include also the use of nanometric Al, in addition to micrometric sized Al, in order to study the effects of Al size to reduce or eliminate surface agglomeration and thus promote single particle combustion. In particular, we will consider different powders: Al-Flakes (ave. diam. 50 μm); Al-Spheres (ave. diam. 30 μm); Al-Medium (ave. diam. 2.5 μm); and Al-Alex (ave. diam. 0.17 μm).

Typically, the composite propellants are constituted by 17% (HTPB or PPG or PEG) binder, 68% ammonium perchlorate (AP) and 15% aluminum (Al). Each propellant is based on a bimodal AP size distribution: coarse particles (80%) in the range 140–160 μm, and fine particles (20%) in the range 70–80 μm.

The acronyms of studied propellants are reported in Tables 1 and 2.

Table 1
First series of propellant formulations

Propellant	Al powder	Al powder nominal size (μm)	Binder
P_1	Alex	0.17	HTPB
P_1/x1	Alex	0.17	HTPB + KR12 disperdent
P_1/x2	Alex	0.17	PPG
P_5	Spheres	30	HTPB
P_1/b20	20% Alex 80% Flakes	0.17 + 50	HTPB
P_3/d20	20% Medium 80% Flakes	2.5 + 50	HTPB

Table 2
Second series of propellant formulations

Propellant	Al powder	Al powder nominal size (μm)	Binder
P_06/x1	μ-Flakes	50	HTPB
P_06/x2	μ-Flakes	50	PEG
P_06/x3	μ-Flakes	50	PPG
P_06/x4	μ-Flakes	50	PEG + double reticulant
P_06/x5	μ-Flakes	50	PEG(50%)/PPG(50%)

3. Burning rate measurements

Propellant samples ($4.5 \times 4.5 \times 30$ mm^3), whose formulations are summarized in Tables 1 and 2, are burned in a nitrogen-flushed window bomb in order to measure the steady burning rate. Samples are ignited by a hot nickel–chrome wire. Pressure is kept constant during the whole combustion process with a feedback pressure control system. The burning rate is measured in the range 1–70 bar, using a high-speed images technique. No significant difference is observed on the burning rate of mono-modal and bi-modal propellants containing 50 and 30 μm Al particle size. Only formulations containing nano-particles exhibit significantly higher burning rates, as shown in Fig. 1(a). By replacing a fraction of $Al_{50 \mu m}$ with the same amount of $Al_{0.17 \mu m}$, the burning rate increases. The binder effect is shown in Fig. 1(b), where samples made of PPG or HTPB + disperdant (KR12) exhibit improved performances.
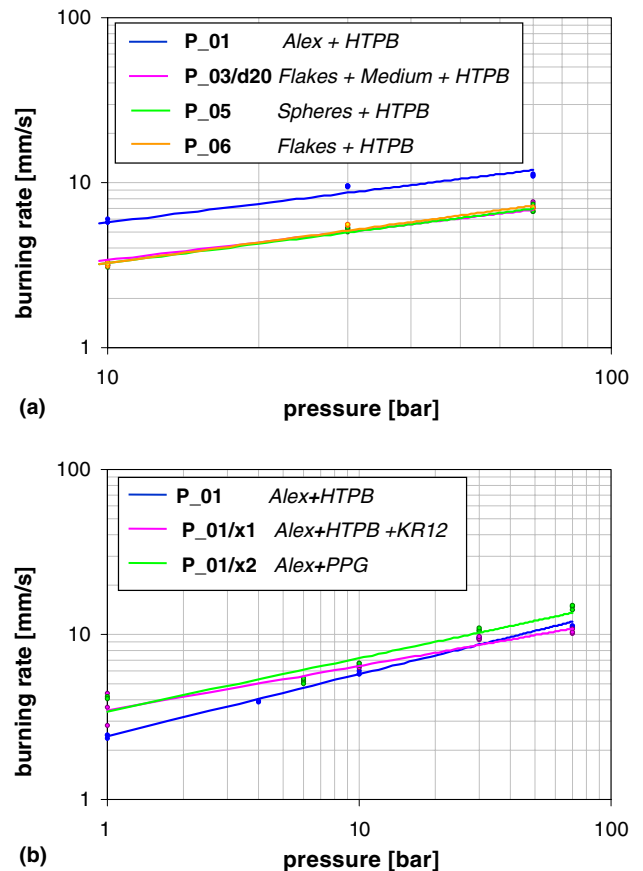

Fig. 1. (a) Burning rate versus pressure for propellant with different Al size. (b) Burning rate versus pressure for propellant with different binders.

4. Residue collection and treatment

The combustion residues were collected in a chamber pressurised with nitrogen and equipped by a plexyglass vessel, having an ice layer inside. This ice layer produces an efficient quenching of collected ashes, falling down for gravity into water formed during combustion, and it protects the glass against flame and keeps the pressure gradient low [5]. The sample is positioned in the centre of the plexyglass vessel, supported on the top by a sample holder. It is ignited by a Ni–Cr wire crossed by electric current and it burns from down to top (see Fig. 2(b)). The internal pressure is kept constant during the burning process, thanks to a retroactive control exercised by electrovalves (see Fig. 2(a)).

After combustion, the mixture of water and residues collected in the vessel is filtered to separate water from all size ashes. Then, they are dried, weighted and treated by aqueous HCl to eliminate the metallic fraction. This technique is useful to determine the metallic fraction in a quantitative way, by comparing the weights of HCl treated and untreated samples. All the weights are normalized to the original amount of metallic Al, present in the propellant sample (15% of its total weight), as the amount of residues depends on the propellant original formulation. The metallic aluminum into ash represents the uncombusted fraction and its presence suggests an incomplete burning process [6].

Figs. 3(a) and (b) show different results: the lower metallic Al amount is observed with nano-sized powder.
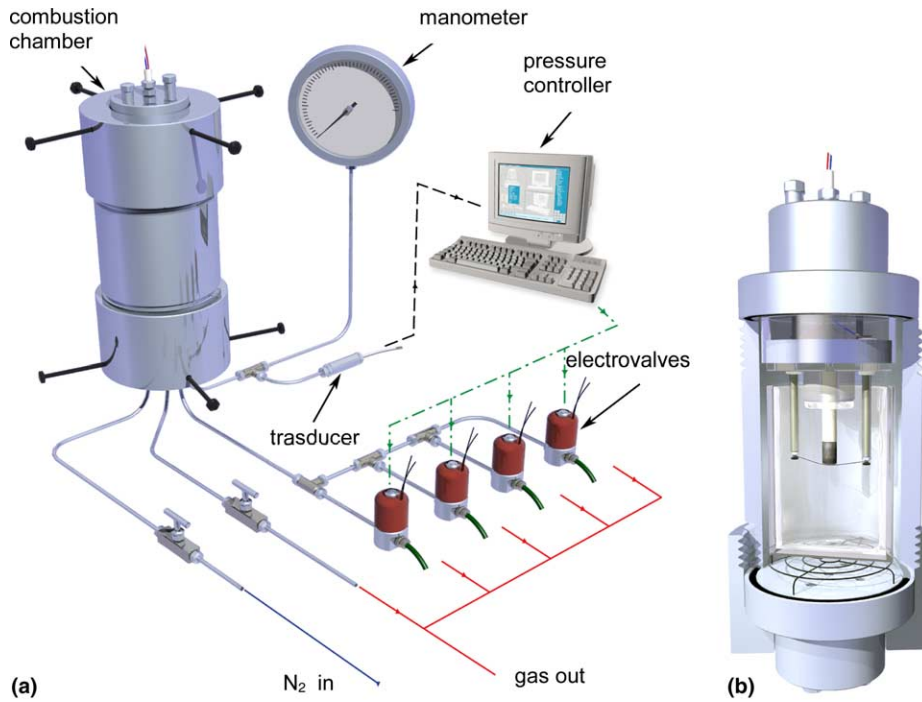

Fig. 2. (a) Scheme of the residue collector. (b) Cross-section of the combustion chamber with vessel, sample holder, sample and ignition wire.
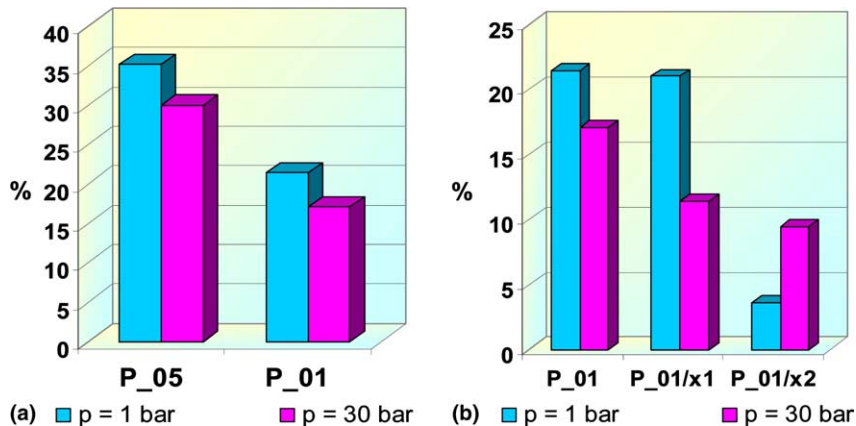

Fig. 3. (a) Different Al amount in residues for different original Al-size. (b) Different Al amount in residues for different binders.

Even lower metallic Al amount is observed by using PPG binder. It is expected that the effect of pressure is to improve the combustion efficiency by lowering the uncombusted Al fraction.

5. XPS analysis

XPS has been used to measure the residue composition and to quantify the atomic concentration of chemical elements contained in the residues. The spectrometer is a PHI-mod. 5500, with monochromatized Al source for X-ray production. The spectra have been taken at 300 W, with a neutralizer for insulating samples. This technique concerns of an X-ray beam impinging on a solid surface and causes the emission of photoelectrons. These photoelectrons, coming from a shallow surface (within about 10 nm), carry the information on the energetic atomic level of the original atomic species. The relative number of collected electrons is related to the relative abundance of the atomic species present on the surface.

The bulk composition (metallic Al/oxide Al) is better investigated by XRD. In spite of this, XPS allows to obtain very interesting results: Table 3 shows the atomic concentration (% atomic) data for P_05, P_01, P_01/x1 and P_01/x2 residues, obtained at different pressures.

Carbon comes from the pyrolysis process and is partially oxidised. Aluminum is mainly detected as Al oxide; metal Al does not appear in surface analysis as it is present in the core of agglomerates. Chlorine is coming from AP decomposition and it remains entrapped into the agglomerates.

The residue chemical composition is affected by the initial propellant formulation, in fact the PPG binder results to contain less carbon than HTPB [7]. Moreover, the higher alumina (Al_2O_3) concentration, the lower carbon is. This is an indication of the oxidation efficiency.

6. XRD analysis

XRD spectra were collected step-wise using Cu Kα radiation on a computer controlled Philips X′ Pert

Table 3
XPS atomic concentrations of combustion residues

at.%	Pressure (bar)	C1s	O1s	Al2s	Cl2p
P_05	1	17.4	46.8	30.2	2.4
P_05	30	16.3	45.7	36.2	1.3
P_01	1	10.4	49.7	38.2	1.4
P_01	30	19.4	45.1	34.0	1.1
P_01/x1	1	17.0	46.1	36.2	0.6
P_01/x1	30	22.3	46.1	29.0	2.6
P_01/x2	1	8.6	49.6	39.3	2.5
P_01/x2	30	11.1	48.6	39.4	0.7

Table 4
XRD crystalline fractions of combustion residues

Crystalline fraction of identified phases					
Propellant	Pressure (bar)	Al^0	γ Al_2O_3	$\delta^*Al_2O_3$	α-Al_2O_3
P_01	1	3.6%	56.7%	37.4%	2.4%
P_01	30	1.5	57.2	37.7	3.6
P_05	1	71.9	16.70	9.0	2.4
P_05	30	9.8	48.4	40.0	1.8

Table 5
XRD crystalline fractions of combustion residues after treatment with HCl

Crystalline fraction of identified phases				
Propellant	Pressure (bar)	γAl_2O_3	$\delta^*Al_2O_3$	α-Al_2O_3
P_01	1	64.3%	33.4%	2.3%
P_01	30	53.9	40.7	5.4
P_05	1	52.2	32.6	15.2
P_05	30	60.3	37.9	1.8

PRO diffractometer, equipped with a secondary curved pyrolytic graphite monochromator, in the 5–125° 2θ angular range, with 0.02° steps and 15 s counting time.

The results of the X-ray powder analysis relative to the combustion products, untreated and treated with aqueous HCl, are summarised in Tables 4 and 5 [8,9].

From the composition point of view all the residues contain qualitatively the same inorganic phases: γ-Al_2O_3, δ^*-Al_2O_3, α-Al_2O_3 and, only for non-treated samples, metallic aluminum. The first two phases are transition metastable aluminas and the third one is stable corundum.

The main result is the low metallic residue content in P_01 sample, which decreases by increasing pressure. This suggests a more efficient burning process with small size aluminum powder. As a confirmation of a good sample oxidation, a global oxide high concentration is corresponding.

7. SEM observations

The used microscope is a Cambridge Stereoscan 360 equipped with a LaB_6 filament. The size of the condensed combustion products depends on: the initial aluminum powder size; the nature of the binder; the burning pressure. After burning, the combustion residuals mainly result in almost spherical particles having a shield of alumina and, sometimes, a metallic Al core.

Fig. 4 puts in evidence the size of propellant residues with different original Al; the sample containing nano Al presents smaller residue size.
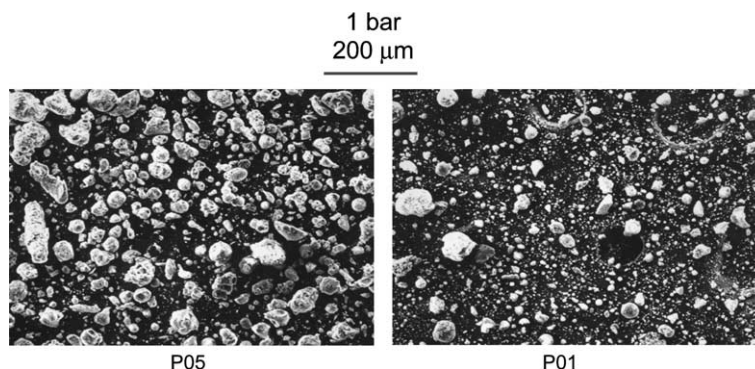
Fig. 4. SEM micrographies (100×) of P_05 and P_01 propellant residues: Al size effect. Fig. 5 puts in evidence the dependence on the binder; the sample made of PPG shows small residues size; but the sample made of HTPB + disperdant (KR12) shows, on average, even smaller particles.
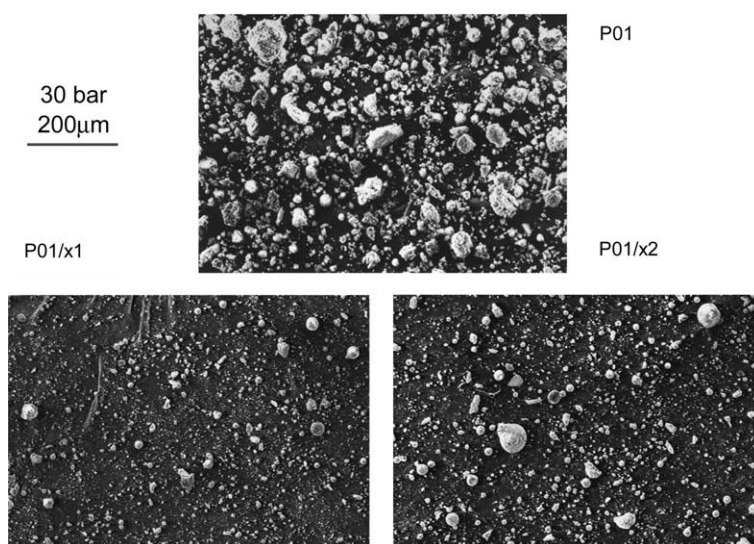

Fig. 5. SEM micrographies (100×) of propellant residues, P_01, P_01/x1 and P_01/x2: binder effect.

8. Conclusions

A multidisciplinary approach was carried out to determine both the burning rate and some chemico-physical properties of propellants and burning products. This gave us the opportunity to correlate structure and chemical composition to ballistic properties. New formulations and testing of rocket solid propellants, obtained by introducing nano-sized Al powders and a no-standard binder like PPG, lead to increase the burning rate by a factor of two. The peculiarities of PPG, to be easily degraded during the combustion process, to give mainly gas-phase products and little solid carbon residues, have the effect to limit Al particle agglomeration. This behaviour allows an efficient surface combustion process to take place. This is confirmed both by the small size of residues and by the low Al/Al_2O_3 ratio, resulting from microscopy and XRD characterisation (see Fig. 5).

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