Coating nano-sized aluminum to improve solid rocket propellant performance

A. Reina, T.I. Gorbenko**, I. Krawiec*, G. Colombo*, and L.T. DeLuca**
**Politecnico di Milano, Aerospace Science and Technology Department, SPLab*
34 Via La Masa, 20156 Milan, Italy
***Tomsk State University,*
36 Lenina pr., 634050, Tomsk, Russia

Abstract
In order to improve dispersion degree of nano-fuel in binder matrices and to increase the propellant performance, coating of aluminum particles with HTPB, Viton, SUREL or 8-hydroxyquinoline is considered. The quality of coating is verified by TEM visualizations. DSC/TG analyses show that the use of HTPB leads to the maximal oxidation degree among the coated powders. The same powder used in HTPB/AP propellants causes a burning rate enhancement up to 26% at 40 bar with respect to uncoated ALEX™ containing composition. The most effective coating for SKDM-80/AP-based propellants is 8-hydroxyquinoline, considering burning rate (+ 26%), and condensed combustion products (-45%).

Nomenclature

Acronyms

ALEX	ALuminum EXploded
AP	Ammonium Perchlorate
CCP	Condensed Combustion Products
DSC	Differential Scanning Calorimeter
EEW	Electro Explosion Wire
H-ALEX	HTPB coated Alex
HTPB	Hydoxyl-Terminated PolyButadiene
NAp	Not Applicable
NAv	Not Avaliable
PBAN	PolyButadiene AcryloNitrile
SKDM-80	Russian used inert binder
TEM	Transmission Electron Microscope
TGA	ThermoGravimetric Ananlyses
XRD	X-Ray Diffractometer

Greek Symbols

µAl	Micrometric aluminum
Δm	Mass difference, %
ΔH	Heat released, J/g

Roman Symbols

a	Pre-exponent of the Vieille law
n	Ballistic exponent in the Vieille law
nAl	Nanosized aluminum
p	Pressure, bar
r_b	Burning rate
T_{onset}	Oxidation onset temperature, °C
z	Amount of CCP, %

1. Introduction

Solid rocket propellants are generally used in space and defense applications. The most common formulation involves ammonium perchlorate (AP) as oxidizer, a polymer, such as HTPB or SKDM-80 (its Russian equivalent) as inert binder and micrometric aluminum (µAl) as fuel. In the last years progress in technologies made available a new class of metallic powders characterized by very small size, and thus very high specific surface: nanopowders. Nanoparticles show different chemical and physical properties with respect to larger scale materials, making them appealing in a wide number of industrial fields, from cosmetics and pharmaceutics to magnetic fluid, efficient catalyst, high-toughness ceramics, and so on. Because of their enhanced reactivity, nanosized powders are quite attractive also for energetic systems and for space propulsion applications [1][2]. Aluminum nanoparticles (nAl) were tested to ignite much earlier than µAl powders, even below their melting point [3], and burning time was estimated in the order of the milliseconds or even lower for nanosized powder dust experiments in air [4].

Nevertheless, together with desirable properties, nanometric particles are characterized also by different surface interactions with respect to bulk materials, resulting in handling difficulties because of the tendency to form clusters that hinder the complete exploitation of nano-composites potential. Cold cohesion phenomenon, or clustering, is strictly connected to Brownian motion [5][6]: it results in a 3D displacement, that increases decreasing particle size, augmenting the possibility of approach and collision. Moreover with close packing models, it was demonstrated that for particles of 100 nm the 3D displacement is higher with respect to the mean distance between particles, even for quite dilute formulations. Due to the high specific surface characterizing nanoparticles, Van der Waals attractive forces are quite relevant and so clusters formation is promoted.
Many approaches have been proposed to mitigate the cohesion phenomenon, ranging from ultrasound to mechanical solicitations to pre-dispersion in solvents. Nevertheless it still remains an open point. In this work a strategy involving particle surface modification is considered: in order to improve the dispersion degree of nanoparticles coating with various materials is proposed. This strategy was selected because it has other positive effects: polymeric coating can prevent active aluminum decrease due to the ageing and can improve propellant manufacture and castability.
For powders to be added in HTPB-based propellants the same polymer used as binder is considered for coating, while for ALEX^{TM} to be employed in SKDM-80 containing formulations a comparison between three different materials is carried out: Viton, SUREL or 8-hydroxyquinoline.
First a characterization of the powders is performed: TEM analyses show the quality of the coating while DSC/TG analyses are considered to evaluate the oxidation of powders in air. Then a ballistic characterization has been carried out on propellants containing ALEX^{TM} with the various coatings and the 2 different kinds of inert binder (HTPB and SKDM-80). Finally, for some of the propellants, condensed combustion products (CCP) are collected and analyzed using a X-Ray Diffractometer (XRD) in order to determine their composition.

2. State of the art

Up to now the most used fuel in composite solid rocket propellants is micrometric aluminum, because it represents the best compromise between density, safe handling, cost and long term stability. It allows a typical 15 s increase of specific impulse and density is 4 % higher with respect to non-metalized formulations , while the burning rate is only slightly modified [7]. Nevertheless µAl suffers from the known limitation of metal combustion: as many other metals it is spontaneously protected to external oxidation by a surface oxide coating hindering ignition and inhibiting combustion of the inner elemental metals. Ignition temperature is connected to surrounding atmosphere and operating conditions, but for the micrometric powder in principle it is necessary to reach 2300K, the melting temperature of alumina [3]. Moreover, production of agglomerates, at or near the propellant surface when it burns in the combustion chamber of a solid motor, causes a reduction in the theoretical specific impulse up to 3% [8].
A possibility to overcome these limitations is given by the increased reactivity of nanoparticles. First studies on nAl application to solid propellants go back to the ‘80ies: Ivanov [9] tested nAl produced by EEW, while Barbee [10] concentrates on multi-layer packs of nano-scale metal mirrors. A remarkable increase in burning rate, up to 100% with respect to corresponding formulations containing µAl was found in lab-scale investigation. Similar results were obtained in more recent years by Dokhan and co-workers [11][12] testing AP/PBAN-based propellants. In these works the burning rate enhancement was correlated to a combustion flame closer to the surface and thus increasing the conductive heat feedback.
Moreover the nAl containing formulations are characterized by different aggregation-agglomeration mechanism: condensed combustion products size is reduced and thin flakes are seen to leave the surface [13]. This can be connected to the higher reactivity of the material that can quickly ignite and does not remain melted on the surface to create new bigger structures.
Unfortunately the substitution of µAl with nAl presents also drawbacks, mainly connected to the increase in viscosity of the uncured preparation, leading to manufacture and castability problems [14] and to the decrease of active aluminum content [15], leading to a lower ideal specific impulse. Moreover clusters formation hinders the complete development of nanocomposites potential.
In order to mitigate cohesion phenomenon different mechanisms were proposed: sonochemistry [16], high energy mechanical systems [17] or pre-dispersion in a solvent [18] are probably the most exploited strategies. Chemical methods are often used to disperse and stabilize nanoparticles in nanocomposite, sometimes together with the physical techniques previously mentioned. Modification of the surface to fight agglomeration or to functionalize nanoparticles is an important chemical challenge that can contribute to the exploitation of the unique features nanocomposites possess. Various strategies, that can also be combined, have been proposed to modify nano-metals surface [19]: organosulfur compounds, like thiols and disulfides can be deposed on particles with solvents or can be added directly to the solution with precursor. Amine as well can be used, but the bond with metal is weaker with respect to organosulfur compounds. In order to modify metal oxides, phosphonate has been studied because of the connection through the oxygen of the oxide. The use of catechol to improve connection between a metal oxide and a

polymer is reported in [20]. The bond between oxide and polymer is created through –OH groups and through the free electrons in the aromatic ring.
In the last decade characterizations of coated nAl from the energetic point of view started to appear in scientific literature, considering the fluoropolymer Viton, stearic acid or other organic compound to perform the coating [21][22]. The most important advantage of particles coated with an organic layer is the higher combustion enthalpy, with respect to standard ALEX^{TM}. The main drawback is the lower active aluminum content of the fresh powder, even if it is worth to notice that some of the investigated coatings can prevent a further oxidation of the aluminum both in dry and wet atmosphere. The same protective effect of coating has been verified also using HTPB [23][24].

3. Coated ALEX^{TM} and propellants

In order to improve the dispersion degree of nAl in solid propellants and to improve the overall ballistic properties, ~~the~~ coating of ALEX^{TM} with various material is proposed. The first considered is HTPB. Coated powders are obtained with 1% of polymer dissolved in mineral spirit, using acetylacetone as coupling agent.
A series of 4 HTPB/AP based propellants, obtained with a standard lab-scale manufacture procedure, is considered in this work. All the formulations share the same nominal composition reported in Table 1, but differs from the kind of aluminum used: HTPB coated powder (H-ALEX) is compared with uncoated ALEX^{TM} and with standard 30 μm aluminum. A fourth formulation contains 9% μAl and 9% H-ALEX.

Table 1 : Standard composition of HTP-based propellants.

Material	Nominal size, µm	Mass Fraction, %
Coarse AP	200	58
Fine AP	5-10	10
Aluminum	Various (0,1 or 30)	18
Binder	NAp	14

A second series of propellant is obtained using 15.8% of SKDM-80 as binder, a mono-modal AP distribution, but comparing two different size (fine < 50 µm and coarse 165-315 µm) and 15% of three differently coated ALEX^{TM}: A1, presenting 1% of organofluorine coating (Viton), A2, obtained with 1% of urethane rubber (SUREL), and A3 coated with 0.5% of heterocyclic organic compound (8-hydroxyquinoline). Details of the tested formulations are provided in Table 2.

4. Experimental set ups and procedures.

The first step of the analysis consists in powders characterization. A direct visualization of the quality of the coating is possible with TEM analyses. For this purpose a FEI QUANTA 200 3D instrument is used. DSC/TGA analyses were carried out using a NETZSCH STA 409 PC/PG set up. 6-7 mg of powders are heated up to 1000 °C at 10 °C/min under an air flux of 190 ml/min.
In order to measure the burning rate of solid propellants, strands of 30 mm were cut from the batch and treated in order to inhibit lateral combustion. Tests were performed in a closed vessel over a pressure range from 1 to 60 bar, using N_2 as pressurizing gas. Combustion events were recorded through a high-speed camera, then post-processed by an automated proprietary software, and finally fitted according to the standard Vieille's law:

$$r_b = a\,p^n \qquad \textbf{(1)}$$

In order to collect combustion residual tests were carried out in air at atmospheric pressure on a textolite substrate. The amount (z) of condensed combustion products (CCP) is determined considering the ratio between the mass deposited on the textolite and the mass of the initial sample. CCP are then analyzed with x-ray diffractometer (XRD) in order to find the composition.

Table 2 : Composition of SKDM-based propellants.

Propellant label	**AP**	**Aluminum**
P- SKDM1	Fine	A3
P- SKDM2	Fine	ALEX^{TM}
P- SKDM3	Coarse	ALEX^{TM}
P- SKDM4	Fine	A1
P- SKDM5	Fine	A1 + $SnCl_2$
P- SKDM6	Coarse	A3
P- SKDM7	Coarse	A3 + $SnCl_2$
P- SKDM8	Coarse	A1
P- SKDM9	Coarse	A2

5. Results

The quality of the coating and its effect on particles was evaluated through TEM analyses. In the analyzed samples, single particles well coated are visible (Figure 1 (a)) together with small clusters of particles that evidence the gluing effect of the coating. In Figure 1 (b) it is possible to see two particles already sintered and a third one stuck to the others by means of coating.

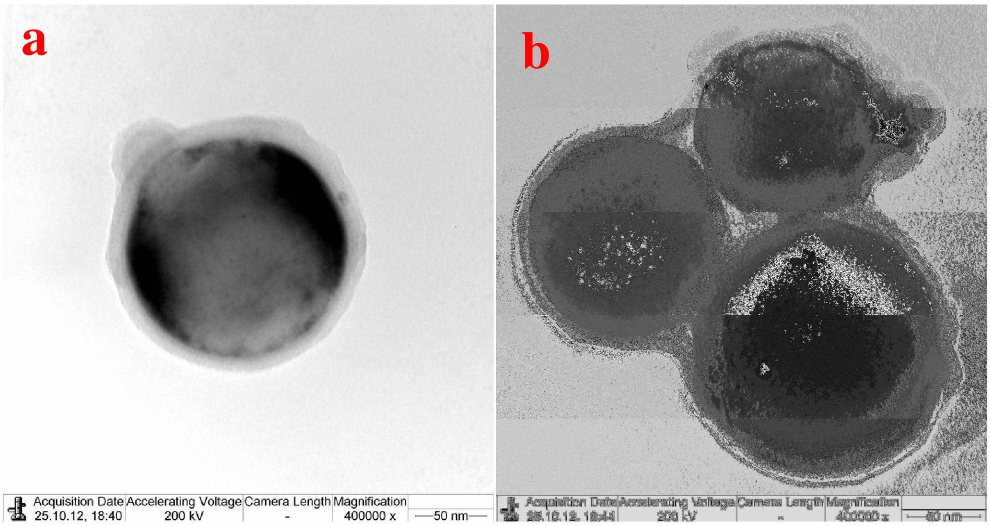

Figure 1 : TEM of ALEX^{TM} coated with 1% HTPB; single particle (a) and small cluster (b). Magnification: 400000X.

Typical DSC and TGA curves are reported in Figure 2 for ALEX^{TM} coated with HTPB. The obtained reactivity parameters are listed in Table 3.

Table 3 : Reactivity parameters for ALEX^{TM} coated and uncoated powders.

Reactivity parameter	ALEX^{TM}	H-ALEX	A1	A2	A3
Δm_1 [%]		-3	-9.5	-2.7	-2.3
T_{onset1} [°C]	579	581	595	580	584
Δm_2 [%]	+ 31	+ 24	+ 16	+ 23	+25
ΔHox_1[J/g]	3039	2395	2031	2403	2601
Δm_{tot} (up to 1000°C) [%]	+ 59	+ 61	+ 34	+ 49	+56

All of the coated powders have a similar behavior; furthermore the plotted curves are similar to the ones obtained for uncoated ALEX^{TM} with onset of oxidation at about 580 °C. The only differences are visible at relatively low temperature, before the oxidation starts: on the DSC curve a small exothermic peak appears at about 200°C. At the same time on the TGA curve a mass reduction indicates as possible cause for the heat released, the coating decomposition. This mass loss is particularly pronounced in case of Viton-coated powder, reaching -9.5%. In this case other phenomena can concur in reducing mass, such as evaporation of residual solvent or desorption of adsorbed gas.
For all the analyzed powders a first oxidation peak is clearly recognizable and appears before the aluminum melting point (660 °C). After the melting point, at about 800-900 °C a second, less intense peak appears, confirmed also by the mass gain shown by TGA curve. This two-stage behavior can be related to the periodic cracking of the oxide shell covering the particle metal core [25] or to the formation of AlN in the second stage [26].

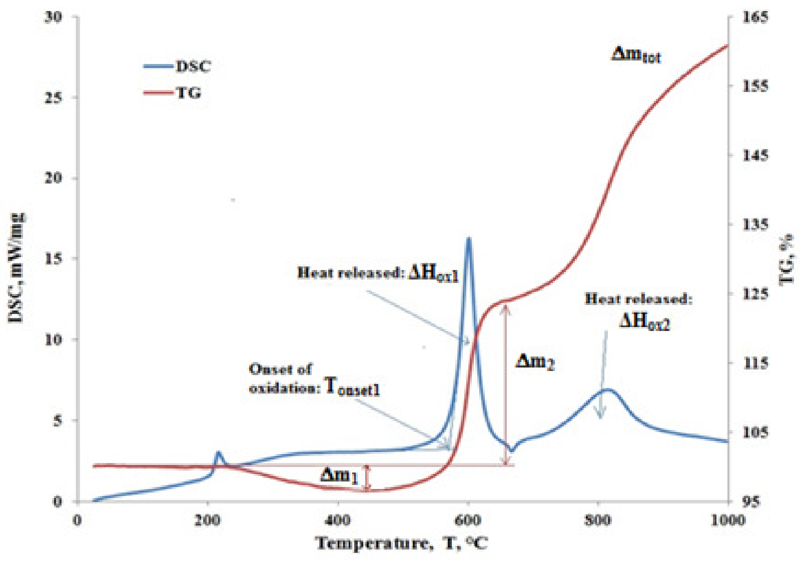

Figure 2 : DSC/TGA curves for ALEX^{TM} coated with HTPB.

Burning rate of the propellant containing 18% of H-ALEX was compared with the ones of the propellant with the same amount of ALEX^{TM} and with the 18% µAl containing one. Considering the bulk density of nAl and the consequent difficult in handling the compound during the manufacture, burning rate was investigated also for a propellant containing a mixture of µAl and nAl in order to find a good compromise between increase in burning rate and manufacturability. Results are shown in Figure 3 and the corresponding Vieille law coefficients are listed in Table 4.

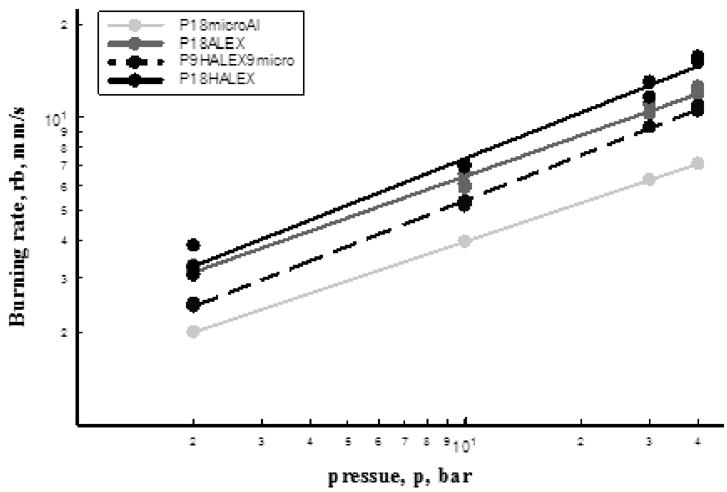

Figure 3 : Steady burning rate for 18%Al containing propellant.

Nanoparticles in solid propellants lead to an enhancement of r_b up to 72% at 40bar. Pressure sensitivity increases as well, as it is possible to deduce from the ballistic exponents listed in Table 4. The burning rate enhancement provided by H-ALEX is visible in the whole investigated range of pressure; at 40 bar r_b increases of 26% with respect to ALEX^{TM} containing propellant and of 117% with respect to the baseline. As drawback, pressure sensitivity increases as well passing from 0.42 for µAl containing propellant to 0.50 if H-ALEX is used. The ballistic exponent remains relatively high even if H-ALEX is mixed with µAl. Nevertheless the increment in burning rate obtained with the mixture µAl/nAl is about 65% at 40bar.

Table 4 : Coefficients of the Vieille law for the baseline (P-18µAl) and for the formulations containing nAl: comparison with 18% ALEX^{TM}, 18% H-ALEX and a mixture 9% µAl/ 9% H-ALEX.

Propellant	a	n
P - 18µAl	1.50 ± 0.03	0.42 ± 0.01
P – 18ALEXTM	2.31 ± 0.07	0.45 ± 0.01
P – 18H-ALEX	2.32 ± 0.12	0.50 ± 0.02
P – 9H-ALEX/9µAl	1.73 ± 0.03	0.49 ± 0.01

Solid propellants containing SKDM-80 as binder were first tested in air at ambient pressure in order to collect the condensed combustion products. The ratio between the residual and the initial mass (z) is presented in Table 5 together with the burning rate.

Both for compositions containing coarse and fine AP, burning rate results higher using coated powders, even if it is worth to notice that for P-SKDM4 and P-SKDM5 combustion is not stable enough to be measured. Condensed combustion products of all the formulations containing ALEX^{TM} coated with the heterocyclic organic compound result reduced: in particular, considering AP coarse containing propellants, z is 19% lower with respect to P-SKDM3 and 45% lower if tin chloride is added. P-SKDM8 burns steadily, but burning rate is lower with respect to the corresponding formulations containing uncoated ALEX^{TM} and the amount of residual is 29% higher. This effect can be correlated with data obtained from DSC/TG analyses: the onset of oxidation occurs at higher temperature with respect to the other powders.

Results obtained with XRD are listed in Table 6 for coarse AP containing propellants.

Combustion tests in nitrogen atmosphere up to 60 bar were performed for formulations P-SKDM1 and P-SKDM5. Results by the standard Vieille law are presented in Table 7.

Table 5 : Burning rate at 1 bar and amount of condensed combustion products for SKDM-80 containing solid propellants.

Propellant label	rb, mm/s	z, %
P- SKDM1	1.4±0.1	6.5
P- SKDM2	1.3±0.1	7.1
P- SKDM3	1.5±0.1	10.0
P- SKDM4	Unstable burning	NAv
P- SKDM5	Unstable burning	NAv
P- SKDM6	1.9±0.1	8.4
P- SKDM7	2.0±0.1	4.9
P- SKDM8	1.4±0.1	12.8
P- SKDM9	1.6±0.1	12.2

The propellant containing ALEX™ coated with Viton presents lower regression rate over the whole investigated range of pressure, in particular if $SnCl_2$ is added. In this last case pressure sensitivity is lower, as can be seen by the ballistic exponent reported in Table 7.

6. Conclusions

In order to improve dispersion degree of nanosized aluminum in binder matrices and to increase the overall propellant performance, coating of the particles with various material is proposed. In HTPB/AP-based solid propellants using the same polymer that acts as binder to coat ALEX™ leads to an increase in burning rate up to 26% at 40bar, with respect to the same formulation containing the uncoated powders and to an enhancement of 117% with respect to the µAl containing formulation.
In SKDM-80/AP-based solid propellants, nAl coated with Viton, SUREL or 8-hydroxyquinoline are compared. Combustion tests show that the most effective coating is provided by the heterocyclic compound, that can grant increase in burning rate and reduction of condensed combustion products for both fine AP and coarse AP containing formulations. Doping the same formulation with $SnCl_2$ allows a further reduction of the residual of 45% with respect to the formulation containing uncoated ALEX™.
The powder coated with organofluorine compound is not so effective in burning rate enhancement, and condensed combustion products are higher. Nevertheless the propellant containing coarse AP Viton-coated powder and $SnCl_2$ shows a quite low pressure sensitivity.

Acknowledgment

This work has partially been supported by grant of Ministry of Education and Science of Russian Federation, Agreement № 14.B37.21.1828.

Table 6 : Condensed combustion products composition for coarse AP containing solid propellants.

	Coating for Alex					
	8-hydroxyquinoline		**SUREL**		**Viton**	
Phase composition (XRD), volume fraction, %	$Al_{2.78}O_{3.65}N_{0.35}$ (cubic)	8.9%	–	–	$Al_{2.78}O_{3.65}N_{0.35}$ (cubic)	19.2%
	AlN (cubic 225)	6.4%	AlN (cubic 225)	3.3%	AlN (cubic 225)	4.6%
	–	–	–	–	AlN (cubic 216)	5.1%
	$Al_{2.667}O_4$ (cubic)	56.6%	–	–	$Al_{2.667}O_4$ (cubic)	36.2%
	–	–	$Al_{2.667}O_4$ (cubic-1)	2.3%	–	–
	$Al_{2.667}O_4$ (cubic-2)	17.3%	$Al_{2.667}O_4$ (cubic-2)	15%	–	–
	–	–	$Al_{2.667}O_4$ (cubic-3)	66.3 %	–	–
	Al_2OC (Hexagonal)	4.8%	Al_2OC (Hexagonal)	3.9%	Al_2OC (Hexagonal)	15.8%
	Al_2O_3 (rhomb)	4.6%	Al_2O_3 (rhomb)	7.5%	Al_2O_3 (rhomb)	13%
	C (hexagonal)	1.4%	C (hexagonal)	1.7%	–	–
	–	–	–	–	C (cubic)	6.1%

Table 7 : Comparison in terms of burning rate for propellant containing A1 or A3.

Propellant label	**Vieille law**	R^2	Pressure range, **MPa**
P- SKDM1	$1.79p^{0.65}$	0.984	1÷6
P- SKDM4	$1.77p^{0.65}$	0.973	1÷4
P- SKDM5	$3.92p^{0.42}$	0.968	1÷4

References

[1] Teipel, U. 2004. Energetic materials. Wiley.

[2] Dreizin, E.L. 2009. Metal based reactive nanomaterials. In: *Progress in Energy and Combustion Science*. 35,2:141-167.

[3] Trunov, M., M. Schoenitz, M., and E.L.Dreizin. 2005. Ignition of aluminum powders under different experimental conditions. *Propell Explos Pyrot.*30,1:36-43.

[4] Huang, Y., G.A. Risha, and V. Yang. 2007. Combustion of bimodal nano/micron-sized aluminum particle dust in air. *P. Combust. Inst.* 31, 2001:2009.

[5] Iijima, M., and H. Kamiya. 2009. Surface modification and characterization for dispersion stability of nanoparticles in liquid media. *Kona*. 27:119-129.

[6] Kamiya, H., and M. Iijima. 2010. Surface modification and characterization for dispersion stability of inorganic nanometer-scaled particles in liquid media. *Sci Technol Adv Mat*. 11: 119-129.

[7] Price, E.W., and M. Summerfield. 1984. Combustion of metalized propellants. In: *Fundamentals of Solid Propellants Combustion*. Progress in Astronautics and Aeronautics 90:479-513.

[8] Reina, A., F. Maggi, G. Colombo, A. Bandera, and L.T. DeLuca. 2012. Nanosized iron oxide catalysts for solid rocket propellants. Space Propulsion 2012. Bordeaux, France. 5-7 May.

[9] Ivanov, G.V., and F. Tepper. 1997. Activated aluminum as stored energy source for propellants. In: *Challenges in Propellants and Combustion 100 Years after Nobel*. Begell House, NY. 636-645.

[10] Barbee, T.W. 1985. Multilayer synthesis by physical vapor deposition. In: *Synthetic Modulated Structures*. Academic press, NY. 313-337.

[11] Dokhan, A., E.W. Price, R.K. Sigman, J.M. Seitzman. 2002. Combustion mechanism of bimodal and ultra-fine aluminum in AP solid propellants. 38th AIAA/ASME/SEA/ASEE/ Joint Propulsion Conference & Exhibit. Indianapolis, IN, 7-10 Jul. AIAA Paper 2002-4173.

[12] Dokhan, A., E.W. Price, R.K. Sigman, J.M. Seitzman. 2001. The effects of Al particle size on the burning rate and residual oxide in aluminized propellants. 37th AIAA/ASME/SEA/ASEE/ Joint Propulsion Conference & Exhibit. Salt Lake City, UT, 9-11 Jul. AIAA Paper 2001-3581.

[13] De Luca, L.T., L.Galfetti, F. Maggi, G. Colombo, A. Bandera, S. Cerri, and P. Donegà. 2008. Burning of metallized composite solid rocket propellants: toward nanometric fuel size. ESA Space Propulsion: 2nd International Symposium on Propulsion for Space Transposrtation, Heraklion, Crete, Greece.

[14] Popenko, E.M., A.A. Gromov, Yu. Yu. Shamina, A.P. Ilyin, A.V. Sergienko, and N.I. Popok. 2007. Effect of addition of ultrafine aluminum powders on the rheological properties and burning rate of energetic condensed systems. *Combust Explo Scock+*. 43,1:46-57.

[15] Gromov A.A., A.P. Iliyin, V. An, F. Faubert, C. de Izarra, A. Espagnacq, and L. Brunet. 2002. Characterization of aluminum powders I. Parameters of reactivity of aluminum powders. *Propell Explos Pyrot*. 27:361-364.

[16] Gedanken, A. 2007. Doping nanoparticles into polymers and ceramics using ultrasound radiation. *Ultrason Sonochem.* 14:418-430.

[17] Muller, F., W. Peukert, R. Polke, and F. Stenger. 2004. Dispersing nanoparticles in liquids. *Int. J. Miner. Process.* 74,1:S31-S34.

[18] Sandler, J., M.S.P. Shaffer, T. Prasse, W. Bauhofer, K. Schulte, and A.H. Windle. 1999. Development of a dispersion process for carbon nanotubes in an epoxy matrix and the resulting electrical properties. *Polym Commun*. 40:5967-5971.

[19] Neouze, M.A., and U. Schubert. 2008. Surface modification and functionalization of metal and metal oxide nanoparticles by organic ligands. *Monatsh Chem.* 139:183-195.

[20] Malisova, B. 2010. Polymer immobilization to metal oxide substrates through catechol derivatives as surface anchors. PhD Thesis. Univeristy of Chemistry and Technology (VSCHT), CZ.

[21] Gromov, A., A. Ilyin, U. Forter-Barth, and U. Teipel. 2006. Characterization of aluminum powders : II. Aluminum nanopowders passivated by non-inert coatings. *Propell Explos Pyrot*. 31, 5:401-409.

[22] Gromov, A.A., Yu.I. Strokova, and A.A. Ditts. 2010. Passivation films on particles of electroexplosion aluminum nanopowders: a review. *Russ. J. Phys. Chem B.* 4,1:156-169.

[23] Reina, A., A.B. Vorozhtsov, I. Krawiec, M. Morlacchi, G. Colombo, M.I. Lerner, N.G. Rodkevich, and L.T. De Luca. 2013. Effects of HTPB-coating on nano-sized aluminum in solid rocket propellant performance. 44th International annual conference of Fraunhofer ICT, Karlsruhe, Germany, 25-28 Jun.

[24] Krawiec, I. 2013. Dispersion techniques of nano-aluminum in AP/HTPB based solid propellants. M.Sc thesis. Politecnico di Milano.Dipartimento di Scienze e Tecnologie Aerospaziali.

[25] Chen, L., L. Chen, W.L. Song, J. Lv, L. Wang, and C.S. Xie. 2009. Effect of heating rates on TG-DTA results of aluminum nanopowders prepared by laser heating evaporation. *J. Therm. Anal. Calorim.* 96,1:141-145.

[26] Mench, M.M., K.K. Kuo, C.L. Yeh, and Y.C. Lu. 1998. Comparison of thermal behavior of regular and ultra-fine aluminum powders (Alex) made from plasma explosion process. *Combust Sci Technol.* 135: 269-292.