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# Overview of Al-Based Nanoenergetic Ingredients for Solid Rocket Propulsion

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## ABSTRACT

The introduction of nano-sized energetic ingredients first occurred in Russia about 60 years ago and arose great expectations in the rocket propulsion community, thanks to the higher energy densities and faster energy release rates exhibited with respect to conventional ingredients. But, despite intense worldwide research programs, still today mostly laboratory level applications are reported and often for scientific purposes only. A number of practical reasons prevent the applications at industrial level: inert native coating of the energetic particles, nonuniform dispersion, aging, excessive viscosity of the slurry propellant, possible limitations in mechanical properties, more demanding safety issues, cost, and so on. This paper describes the main features in terms of performance of solid rocket propellants loaded with nanometals and intends to emphasize the unique properties or operating conditions made possible by the addition of the nano-sized energetic ingredients. Steady and unsteady combustion regimes are examined.

**Keywords:** nanoaluminum; solid rocket propellant; burning rate; combustion; propulsion; performance.

## BACKGROUND

In energetic applications, such as propellants, pyrotechnics, and explosives, Al is widely used because of its high combustion enthalpy, easy availability, low toxicity, and good stability. Aluminum, whether powders or flakes, is used to increase the energy and raise the flame temperature in rocket propellants (a direct but awkward way to increase specific impulses); it is also added to explosives to enhance air blast, raise reaction temperatures, create incendiary effects, and increase bubble energies in underwater weapons. In rocket propulsion, combustion processes of conventional micron-sized Al ( $\mu\text{Al}$ ) powders proceed relatively far from the propellant surface and do not significantly contribute to the propellant burning rate. On the contrary, ultrafine energetic particles, especially nano-sized ones, are objects characterized by very small size and subsequently very high specific surface area. Thus, they appear very attractive because of their different chemical and physical properties, compared to the corresponding bulk or micron-sized materials. Especially nano-sized Al (nAl) is broadly exploited to improve performance incrementing the burning rate and combustion efficiency of energetic systems, leading to shorter ignition delays and shorter agglomerate burning times with respect to energetic systems containing  $\mu\text{Al}$ . As a matter of fact, the rapid acceleration of research in the area of metal-based reactive nanomaterials can readily be traced back to the development in nAl manufacturing.

In the pioneering experiments conducted in 1959 at the Institute of Chemical Physics (ICP), Moscow, Russia, a remarkable increase of propellant steady burning rates and decrease of the Al combustion condensed products (CCP) sizes were observed

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bulk or micron-sized materials. Especially nano-sized Al (nAl) is broadly exploited to improve performance incrementing the burning rate and combustion efficiency of energetic systems, leading to shorter ignition delays and shorter agglomerate burning times with respect to energetic systems containing  $\mu\text{Al}$ . As a matter of fact, the rapid acceleration of research in the area of metal-based reactive nanomaterials can readily be traced back to the development in nAl manufacturing.

In the pioneering experiments conducted in 1959 at the Institute of Chemical Physics (ICP), Moscow, Russia, a remarkable increase of propellant steady burning rates and decrease of the Al combustion condensed products (CCP) sizes were observed [1-2]. This breakthrough arose great expectations in solid propulsion practitioners. Higher energy densities and faster energy release rates were anticipated with respect to the conventional energetic ingredients in general. The possibility was also foreseen to mitigate the 2P flow performance losses in solid rocket motors (SRM), associated with gas dynamic expansion, by burning nAl powder instead of the conventional  $\mu\text{Al}$  fuel. Furthermore, in combination with the conventional micron-sized energetic materials, nano-energetic materials were shown to allow a more precise control of the energy release rate. This opened the way for a large range of applications, which extends quite beyond the solid rocket propulsion area treated hereunder.

This paper is based on a series of recent book chapter contributions [3-5] and, as such, heavily relies on the corresponding extended reference lists. The paper intends to conduct an overview of the development, present status, and perspectives in the area of solid rocket propellants augmented by nanometals, in particular nAl. In addition to Al-based reactive nanomaterials, appreciable progress has also been made in creating improved high explosive materials, nanocatalysts, carbon nanotubes, and impregnated porous silicon. Technical interests certainly extend over a wide range of applications, but attention is preferably focused on ingredients and propellant formulations used for space exploration propulsive missions. A review was recently offered in [6]. The different production techniques of nano-sized powders are not considered in the present work; the interested reader is referred to the wide literature already available [4,5,7].

For centuries, rudimental forms of solid rocket propulsion were based on black powder, following the fortuitous alchemist activities in China dating as early as ca 220 BC [7]. Significant advances were made in Europe, introducing nitrocellulose (NC)-based smokeless gun propellants, only during the years 1863-1888. Further advances were made at the

Mikhailovskaya Artillery Academy, Leningrad (now Saint Petersburg), Russia, in 1925 (smokeless propellant for rocket shells based on Pyroxylin) and 1933 (Double-Base powder N for SRM) [7]. Decisive advances were made in the USA, introducing castable composite propellants in the framework of the GALCIT program dedicated to Jet Assisted Take-Off (JATO) rockets. In June 1942 Parsons, a self-educated and very eccentric but also imaginative chemist, combining an organic matrix (asphalt) with a crystalline inorganic oxidizer ( $\text{KClO}_4$ ) succeeded in making the first castable composite solid propellant. Composite propellants eventually replaced Double-Base propellants in most rocket applications. The GALCIT project was the start of modern solid rocketry.

But the push toward more and more performance is now at its end, as shown by the flattening curve of delivered Is during the last decades. At least in the Western world, the state-of-the-art in solid propulsion for space exploration is represented by AP/HTPB (Hydroxyl-Terminated PolyButadiene)/Al formulations. Advanced ingredients under study are discussed in [7]. All are far from flight applications. On the opposite, some nano-sized catalysts have been in use for longtime for solid rocket applications [8].

### **NANOMETALS: ENERGY EXCESS?**

Nanoenergetic materials (nEM), energetic nanocomposites, metastable intermolecular composites (MIC), and so on, often based on metal fuels, are a new class of materials featuring nano-sized range and reaction rates higher by orders of magnitude with respect to conventional high energy materials. Nanostructured energetic materials are characterized by nano-scale sizes in at least one dimension. Graphene is a recent example of two-dimensional structure, being a sheet of carbon consisting of few (at most ten) layers of carbon atoms. A conventional classification is often accepted whereby ultrafine particles fall in the range 1000 nm to 100 nm, while nano-sized ones are those in the range 100 to 10 nm. Thus, 100 nm can roughly be seen as the conventional boundary between ultrafine and nano-sized objects. For convenience, the expression nanoaluminum (for example) will be used throughout this paper without distinction between ultrafine and nano-sized particles, although this paper essentially deals with ultrafine particles.

Energetic nanotechnology in general attempts to break the mentioned chemical energy deadlock by pursuing a different approach, i.e., looking not for new molecules but at the “bottom scale”. This new way at the beginning looked revolutionary and, during last two decades,

attracted much attention in many laboratories all around the world. It was initially claimed that nAl formed by EEW (Electrical Explosion of Wires) process has unusual physical and chemical properties, and “has conserved energy which is useful in enhancing the performance of propellants and explosives.” Alex, a well-known commercial form of nAl, was supposed to contain an additional amount of stored internal energy, on the order of 400 cal/g, which is due to nonequilibrium EEW process [9]. This appealing idea was repeatedly verified but no experimental or theoretical corroboration could be found. Today, advantages and limitations are much better understood.

In their first generation [10-30], the common manufacture technique of nEM has been and still is by mechanical mixing of single powders, borrowing from pyrotechnics the traditional approach developed longtime ago: nanoparticles of interest are first synthesized and then embedded into a matrix material. The resulting mixture with other micron-sized components enjoys the large specific surface of the energetic nanoingredient, often a metal powder increasing the reaction rate and decreasing the ignition delay of the whole mixture. About two decades of experimental investigations confirmed improvements in the ballistic properties, but also revealed weak points. In an attempt to avoid drawbacks, new manufacturing strategies have been pursued including:

- Bulk nanostructured energetic materials, whereby nanocomposites mixing is accomplished by combining into a single process nanoparticles synthesis and compound formation [31-33].
- Extension of the EEW production of nanoenergetic materials to two ingredients (typically, two metals) exploiting their combination synergy [34-35].
- Refinement of conventional micron-sized energetic materials ( $\mu$ EM) in order to achieve ultrafine properties via chemical [5] or mechanical [4][37] activation.
- Augmentation of conventional  $\mu$ EM oxidizers performance by introducing new ingredients, such as graphene [38], or manufacture techniques, such as encapsulation [5][39][40].
- Creation of nanocomposite materials along new production techniques. A bottom-up approach based on nano-particles or nano-foils produced from elemental atoms or molecules (including MIC of mixed metal-oxide nanoparticles, sol-gel produced nanocomposites, and nanofoils) and a top-down approach based on refining the bulk materials to achieve nano-

scaled mixing between components (such as the arrested reactive milling or shortly ARM technique). Such as [41].

- Refinement of nanoscale energetic materials by means of coating techniques [42- 44].

Overall, progress is being accomplished along multiple and sometimes intersecting guidelines, with overlapping mechanical, chemical, and manufacture effects.

### BASIC FLAME STRUCTURE MODIFIED BY ALUMINUM POWDER

The stand-off distance for particle burning, usually noticed in the flame zone of  $\mu\text{Al}$  propellants, cannot be seen in the blurred image typical of  $\text{nAl}$  propellants; contrast Fig.1a ( $\mu\text{Al}$ ) with Fig.1(b) ( $\text{nAl}$ ). For the explored operating conditions typical of space launchers, i.e., AP/HTPB-based formulations burning over the pressure interval from atmospheric up to about 7 MPa, Al particle size affects burning according to the following trends [11-17]:

For  $\mu\text{Al}$  propellants, Al particles feature a spacewise distributed burning overlapping the underlying unmetallized flame structure: it starts with an appreciable stand-off distance from the burning surface and it extends much beyond the gas-phase flame thickness. For  $\mu\text{Al}$  burning, most of the heat release occurs far from the burning surface. Thus, the underlying flame structure is affected only to a modest extent in terms of steady burning rate and pressure sensitivity.

For  $\text{nAl}$  propellants, no stand-off distance appears. A significant steady burning rate increase is observed, which is stronger with decreasing  $\text{nAl}$  size over some appropriate range. Typically, the maximum increase is by a factor of two passing from  $\mu\text{Al}$  to  $\text{nAl}$ .

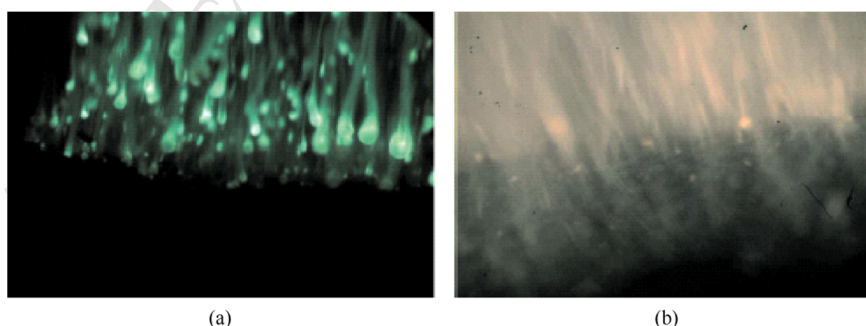


Fig.1 (a) Particle-laden flame zone due to  $\mu\text{Al}$  combustion at some standoff distance from the burning surface at 1 MPa [11]. (b) Fine aggregate emerging on the surface by exudation and reduced transition to spherical agglomerates near the burning surface for a  $\text{nAl}$  propellant at 1 MPa [11].



In this paper, the word agglomeration is reserved for the spherical drops of liquid metal in combustion with an oxide cap, while the word aggregation is reserved for the partially oxidized objects of irregular shape typically seen as precursors of agglomeration [16]. A similar classification was previously used by Glotov et al. [18]. Agglomeration always implies a loss of the initial particle individuality, while aggregation may keep some remnant of the initial particle individuality. Optical measurements of the aggregate formations or agglomerate diameters detaching from the burning surface (incipient agglomeration) can be performed or movies can be analyzed using dedicated software.

Visual analyses performed at the author's SPLab pointed out that the emission of aluminized solid aggregates over the combustion surface of AP/HTPB formulations depends on the propellant microstructure; see Fig.1(a) ( $\mu\text{Al}$ ) and Fig.1(b) (nAl). These aggregates emanate from the propellant, grow on the burning surface, accumulate, and protrude into the gas phase until their detachment [22]. The possibility exists for nAl formulations of in-depth metallic networks forming during propellant manufacturing and storage. This distinctive difference with respect to  $\mu\text{Al}$  can sensibly influence the propellant combustion.

By comparing the growth mechanism of aggregation/agglomeration processes in aluminized formulations, the burning mechanisms of  $\mu\text{Al}$  (Fig.2(a)) vs. nAl-loaded (Fig.2(b)) solid propellants are drastically different. Contrasting burning processes at or near the combustion surface clearly indicates a stronger brightness of the region immediately above the burning surface for nAl vs.  $\mu\text{Al}$  propellants. This fact can be associated with the rapid combustion of nAl in that region, which enhances near-surface heat release, thus increasing the burning rate by increased conductive heat feedback. Overall, the spacewise distributed flames typical of  $\mu\text{Al}$ -loaded propellants are replaced by very short flames typical of nAl-loaded propellants.

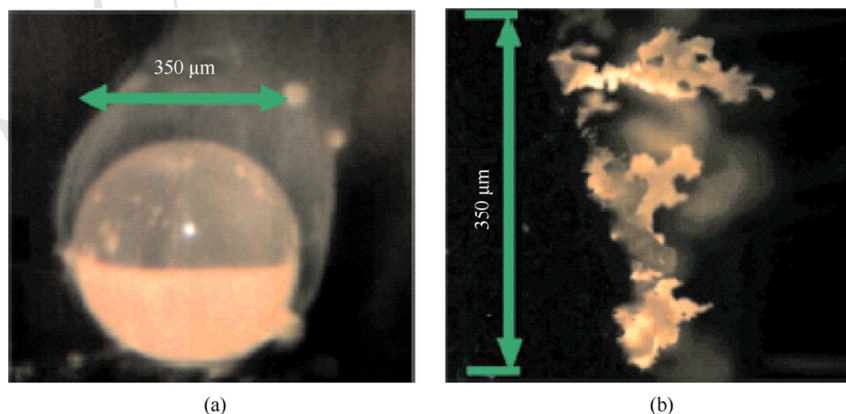


Fig.2 (a) Magnified view of a single spherical agglomerate of  $\mu\text{Al}$  in combustion above the propellant surface following inflammation of aggregates. (b) Oxidized metal flakes emerging from the burning surface of a nAl propellant at 1 MPa [4].

Among the many amazing properties displayed by nano-sized particles, regarding solid propellant applications, two are the basic properties differentiating the ultrafine Al, actually employed in propulsion, from the conventional  $\mu\text{Al}$ : specific surface area and active Al content ( $C_{\text{Al}}$ ). While  $\mu\text{Al}$  particles contain only a minimum amount of natural  $\text{Al}_2\text{O}_3$  coating, nAl is prone to lose active Al content due to the significant volumetric fraction of the natural  $\text{Al}_2\text{O}_3$  coating, since its importance increases with decreasing particle size: for example, the metal content reduces to 50 % for particle sizes around 15 nm. Typical values of  $C_{\text{Al}}$  are at least 98% for  $\mu\text{Al}$  and, say 70-90% for nAl. Chemical and/or mechanical activation as well as surface coating of  $\mu\text{Al}$  particles usually lead to a  $C_{\text{Al}}$  reduction of few %. These losses differ depending on the amount of additives and processing details [7].

In principle, the oxide layer of Al particles can be either amorphous or crystalline depending on the production techniques and processing details such as temperature and duration. For freshly produced Alex by EEW in argon, the native oxide layer is amorphous and uniform with a thickness of about 2.5 nm. But it slowly crystallizes to a larger thickness (say, 7–8 nm) during a storage period of 2–3 years at room temperature [30]. Moreover, the active Al content may dramatically decrease in time depending on storage conditions and aging [4].

### STEADY BALLISTIC PROPERTIES

In most applications, nAl is the implemented energetic ingredient. Many international investigators report that using nAl typically, but not always, involves a significant increase of the solid propellant steady burning rate, while its pressure sensitivity may exhibit disparate effects. This is an extremely important property for SRM, but findings are quite scattered and include all possibilities: increases, decreases, or negligible changes were observed for n.

The different trends noticed among the many experimental results collected from the open literature are likely due to the different flame structure involved in the specific experimental testing, in turn depending on the overwhelming number of parameters controlling metallized solid propellants nanoenergetics: pressure interval, type and mass fraction of ingredients, size and grain size distribution of particles, total solids fraction, kind and details of the binder system, preparation technique and manufacturer of the ingredients, and so on. Quality of the

propellant manufacture is another, not easily measurable, reason for the observed discrepancies.

Under the common operating conditions typical of space launchers, for the wide family of AP/HTPB-based composite propellants [11-17] the steady burning rate vs. BET (Brunauer–Emmett–Teller) area increases up to a factor of about 2, while the associated pressure sensitivity is not significantly affected; see Fig.3. For other AP-based propellants and/or operating conditions, burning rate may increase by even more than a factor of 2 and pressure sensitivity can either increase or decrease.

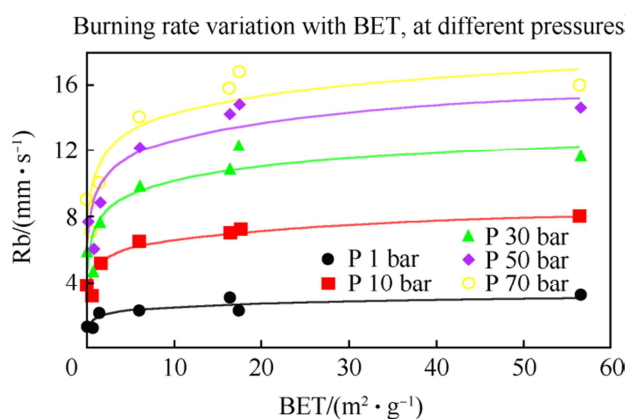


Fig.3 AP-bimodal (54.4% 150  $\mu m$  coarse and 13.6% 75  $\mu m$  fine)/HTPB/Al solid propellants, in mass % 68/17/15. Steady burning rate vs. BET specific surface area, at different pressures and for propellants loaded with monomodal Al powders, showing limited effects for large BET values, above say 10  $m^2/g$  at 10 bar (the discriminating value increases with pressure).

For AP/HTPB-based composite propellants, the systematic analyses by Jayaraman et al. [19-21] was successful in showing how multifaceted the nAl effects can be. By extending the pressure interval and granulometry of solid particles, a complete portray of the ballistic trends could be obtained. In routinely used AP-based propellants, it was confirmed that the presence of nAl increases steady burning rate up to a factor of about 2 and essentially retains the pressure exponent. However, for nonAl and  $\mu$ Al propellants containing fine AP of very small size (5  $\mu m$ ) and coarse AP of very large size (450  $\mu m$ ), the associated plateau burning rate effects are washed out in the corresponding nAl formulations. In the presence of nAl, these peculiar ballistic phenomena show significant changes in the pressure exponent over a range of pressure wider than usual. The results collectively indicate that the nAl propellant steady burning rate is controlled by the near-surface nAl ignition and combustion, which becomes diffusion limited in the elevated pressure range, with low pressure exponents. On the other hand, the predominance of nAl combustion in controlling the steady burning rate is limited (i) when the exposed

areas of the fine AP/binder matrix on the burning surface are restricted, and (ii) when the fine AP particles are too small to hold attached leading edge flames (LEF) [22] and ignite the nAl effectively. Under these circumstances, the burning rate increase of the nAl propellant is marginal.

Innovative HTPB-based solid propellant formulations, loaded with nano-sized metals (nMe) or metal oxides (nMeO), were systematically investigated Pang et al. [24] [25], typically over the pressure range 1 to 15 MPa, with various effects on steady burning rate and pressure sensitivity.

RDX (Cyclotrimethylenetrinitramine)- and HMX (Cyclotetramethylenetetranitramine)-based composite propellants are a source of conflicting trends [31-33]. Self-propagation rates of RDX increase with decreasing particle size, see Fig.4, while this could not be observed for HMX. In addition, for some RDX-based propellants, an abnormal increase of steady burning rate and decrease of the average pressure exponent were observed with increasing RDX particle size [26]. This is probably due to a transition from the standard Piobert's burning mechanism (combustion by parallel layers) to a kind of convective burning mechanism, triggered by coarse particle ejection from the molten propellant surface during combustion.

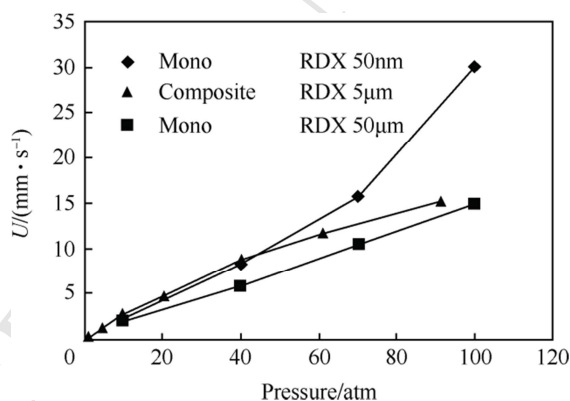


Fig.4 Steady burning rate dependency on pressure of RDX-based formulations showing nRDX monopropellant much faster than  $\mu$ RDX monopropellant and a  $\mu$ RDX-based composite propellant [32].

Concerning advanced ingredients and techniques, in general more work is needed to fully assess their potential. Using bimetallic ingredients [34-35] shows that a good synergy among constituents is indeed possible (Alex+Fe) but not granted (Alex+B); see Fig.5. Replacing standard  $\mu$ Al by mechanically activated Al/PTFE (PolyTetraFluoroEthylene) composites shows that, while Al/PTFE (90/10%) does not significantly affect propellant burning rate,

Al/PTFE (70/30%) increases the pressure exponent from 0.36 to 0.58 [37]. Solid propellants with decorated functionalized graphene [38] exhibit increased steady burning rates with decreased pressure exponents. Likewise, increased steady burning rates with decreased or unchanged pressure exponents are achieved by solid propellants modified via encapsulation techniques [39-40]. A significant increase in steady burning rates with negligible pressure exponent changes is also achieved in burning AP/HTPB-based propellant loaded with Al/Fe<sub>2</sub>O<sub>3</sub> nanocomposite [41]. These approaches offer promising new ways to augment steady ballistic properties.

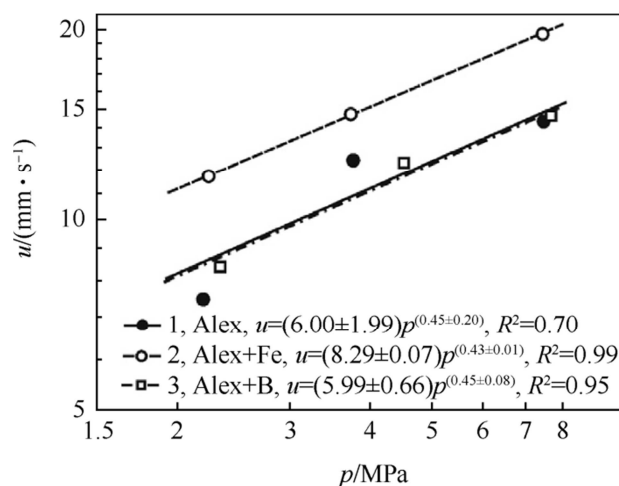


Fig.5 Steady burning rate vs pressure of the indicated Alex+Fe and Alex+B propellants with respect to the reference Alex-loaded propellant [34].

In broad terms, the steady burning rate augmentation commonly observed in nAl composite solid rocket propellants is due to the rapid consumption of nAl particles, with respect to conventional  $\mu$ Al particles, in the immediate vicinity of the combustion surface. This fact is mainly determined by the more intense energy release by nAl particle oxidation completion very close to/above the burning surface, following a kind of prompt partial oxidation at/below the burning surface triggered by condensed phase reactions. In turn, the near surface larger heat release is essentially due to the larger specific surface area of nAl and the subsequent larger surface contact areas with the surrounding ingredients. Other factors affecting nAl performance include particle average size and size distribution, particle aggregation, active Al content, nature of the passivating layer, and additional subtle chemical and physical factors (such as reactive interfaces, intermetallic compounds, crystalline structure, and so on).

With respect to nAl, chemical and mechanical activation of conventional  $\mu$ Al particles are in general less efficient in increasing steady burning rates, but also less demanding in decreasing the active Al content. They offer the advantage of augmented particle reactivity, as testified by a reduced ignition temperature and activation energy. However, the shape of the treated particles may be heavily affected by the activation treatment, and the subsequent effects on propellant packing and burning should be verified.

All considered, no urgency is felt in augmenting ballistic performance of the current composite solid rocket propellant families by using nAl. Larger steady burning rates can often be obtained by other means, e.g., burning rate modifiers, without correlated penalizations. Regarding steady ballistics, at this time the best use of nAl seems to be a small replacement of the conventional  $\mu$ Al load of the propellant charge for the fine tailoring of steady ballistic properties, acceptable EOM viscosity, and reduced smoke exhausts.

### UNSTEADY BURNING

With respect to conventional  $\mu$ Al-loaded composite solid rocket propellants, nAl formulations were shown to feature a stronger resistance to both dynamic extinction by fast depressurization ( $dp/dt$ ) and static extinction by pressure deflagration limit (PDL). Results from experimental campaigns in different laboratories pointed out a distinctive stabilizing effect for nAl containing formulations. The common reason for both effects being the tighter energetic coupling at the burning surface and possible condensed phase activities for nAl formulations.

In qualitative agreement with other results, the presence of nAl can influence the very nature of the propellant combustion wave by:

- Affecting recoil force, via smoothening of burning rate oscillations [10].
- Triggering combustion instability, likely due to nonuniform nAl particle distribution [10].
- Washing out plateau burning [19-21].
- Causing “explosive” ignition, as observed for aluminized composite solid propellants based on ammonium nitrate (AN) and energetic binder (EB) subjected to  $\text{CO}_2$ -laser radiation in air at ambient pressure [28].
- Affecting dynamic response and acoustic damping [29].
- Mitigating self-sustained oscillations near PDL by enriching its frequency content [4].see Fig.7.

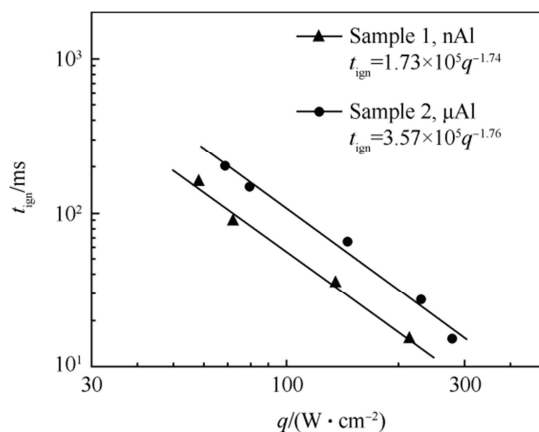


Fig.6 Ignition delay of  $\mu$ Al and nAl aluminized composite propellants versus radiant flux intensity at atmospheric pressure. Propellant composition in mass fractions: 72% AP + 18% Butyl rubber + 10% Al. Radiant source: 600 W Xenon arc image [5].

This array of experimental trends indicates that the exact results due to nAl combustion depend on the many details of the propellant formulation, as already discussed in the previous section. The quality of the propellant manufacture and dispersion of nEM in the propellant matrix (microstructure) are also important.

## IGNITION

All processes involving energetic materials necessarily start with an ignition transient, leading the examined compound from a nonreacting to a reacting state. On one hand, this transient has to occur reliably and only on command for a SRM to function successfully, on the other hand the same transient should be prevented if an unplanned triggering event occurs (known as inadvertent ignition). This matter is of strong interest for practical reasons of safety and requires a good grasp of the relationship between propellant ignitability and hazards response. In fact, the well-ascertained increased reactivity of nEM is accompanied by increased hazards as well.

Ignition delay of nAl-loaded formulations is shorter with respect to  $\mu$ Al formulations; for example, see Fig.6. This is due to smaller particle size, larger specific surface area, thinner oxide layer thickness, and better contact with other propellant ingredients as well as to the intrinsic easier ignitability of nAl powders [27]. Chemical activity of nAl, which promotes heat release in the condensed phase is also pointed out by the minimum slopes of the ignition delay time vs. radiant flux curves. This was observed in many (but not all) tests, because is subject to the many details of the propellant formulation and manufacture. In addition, the lower tempera-



ture of rapid oxidation beginning is confirmed by thermal analysis, although under low heating rates.

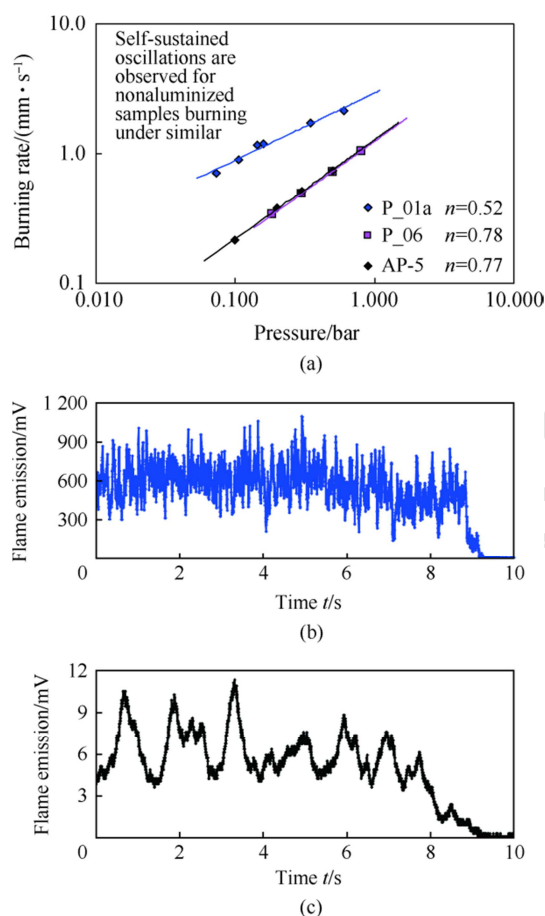


Fig.7 (a) Subatmospheric burning rate versus pressure ( $D_{AP} < 71 \mu\text{m}$ ) showing faster combustion and lower pressure exponent for nAl formulation P\_01a with respect to  $\mu\text{Al}$  formulations (laboratory P\_06 and industrial AP-5) [4]. (b),(c) Experimental traces of flame luminosity near PDL for nAl (high-frequency strong emission, PDL=63 mbar) and  $\mu\text{Al}$  (low-frequency faint emission, PDL=69 mbar) formulations, respectively.

The above interpretation is in qualitative agreement with the image in Fig.2b suggesting subsurface chemical activity for nAl. The trend toward decreasing ignition temperature with decreasing particle size is well proved [4] and goes well below not only the melting temperature of the bulk oxide shell, say 2350 K [6], but also below the typical burning surface temperatures of aluminized composite propellants (say, 900-950 K depending on pressure). This decreasing trend is accompanied by a simultaneous decrease of the Al melting temperature and melting enthalpy with decreasing particle size [6], but this effect is usually negligible for the nAl particles used in actual propellants.



In a more general context, partial or complete replacement of the conventional  $\mu\text{Al}$  by Alex reduces the ignition time by increasing the heating rate in the condensed phase. For example, in the case of the dual oxidizer (AN+HMX) formulation with energetic binder, at ignition the average burning surface temperature was estimated as about 820-930 K with Alex, against 990-1090 K with ASD-4  $\mu\text{Al}$ , for 60  $\text{W}/\text{cm}^2$  of radiant flux. For the same radiant flux, the heating time of the reaction layer is six times shorter for Alex with respect to ASD-4  $\mu\text{Al}$  [28]. However, this large difference could also be the result of different thermal conductivities of the tested propellants.

For the new generation of nEM, bimetallic formulations with 5% Ni seem to offer a promising way out to achieve at the same time good ignitability and higher safety [35]. Not sufficient information is available for other innovative formulations (nanocomposites, graphene, and so on). An interesting remark of general validity is, however, offered in the recent paper by Vorozhtsov et al. [36]: Al ignition is most likely occurring soon after the polymorphic phase change transforming the natural amorphous alumina into a higher density  $\gamma\text{-Al}_2\text{O}_3$  phase. The diffusion resistance of the oxide layer diminishes, and reaction rate accelerates causing ignition.

### VISCOSITY, AGGLOMERATION, SPECIFIC IMPULSE

Increased viscosity and possible damaging of mechanical properties are negative effects associated with the use of nano-sized energetic ingredients. Adding nano-sized ingredients affects the solid propellant manufacture of all formulations containing more than a critical mass fraction of nanoenergetic ingredients. Depending on the specifics of the formulation under consideration, this critical value was estimated in the range 5-10% [5]. A practical way to overcome the slurry processibility difficulties, when resorting to bimodal (fine nAl + coarse  $\mu\text{Al}$ ) mixture, is to implement a C/F ratio of 1:1 for the Al particles. A more comprehensive approach [36] is to coat nanoparticles with organic substances preventing particle aggregation, achieving disaggregation, favoring compatibility with organic binders, and promoting resistance to environmental factors. An instance of optimized HTPB coating for EEW nAl (H-Alex) is discussed in [4][43]. The spontaneous aggregation of nanoenergetic ingredients, for example nAl in [44] and nRDX in [26], confirms the utmost importance in avoiding such effect in order to preserve the positive influence of the implemented nanoenergetic ingredients on the propellant properties.

Regarding CCP and agglomerate size, experimental data confirm that the incipient agglomeration is appreciably reduced for nAl. Likewise, the size of the CCP in quenched samples is appreciably reduced. However, in the open literature, very little is said about the fate of nAl particles passing through the throat area of the gasdynamic expansion nozzle. In addition, with respect to the conventional  $\mu$ Al particles, nAl is appreciably less effective in damping out SRM acoustic instability [29] and its influence on the recoil force [10] is somewhat similar to that observed for subatmospheric burning near PDL [4].

In this regard, since there is no extra energy in the current generation of nAl, no gain in the ideal is can be expected; actually, a drop will take place depending on the amount of nAl inert coating. As to the delivered specific impulse, the  $I_s$  drop could be compensated by the possible reductions of the 2P flow losses; but this has not yet been verified in actual SRM, because of the appreciable particle coagulation taking place in the subsonic and sonic portions of the gasdynamic nozzle.

### SAFETY

Safety concerns all aspects of energetic materials life cycle, including production, handling, transportation, storage, and use. Safety of nMe per se is fully discussed in [4], but limited to a group of powders: Al(Ar), Al(N<sub>2</sub>), Cu(Ar), Cu(CO<sub>2</sub>), Ni(Ar), Zn(Ar), and Fe(Ar). All of them were produced by EEW in the indicated gas and were initially passivated by slow exposure to air. Results are given in terms of: flammability as measured by the ignition delay time by low-energy sources, ESD (electro static discharge) sensitivity as measured by the minimum energy needed for ignition, and hazard classification sorting. The combined results, from flammability tests by a Bunsen burner and spiral wire heating, overall point out Fe(Ar) as the quickest powder to ignite and Cu(CO<sub>2</sub>) as the slowest. Based on the analyses carried out in [4], one can conclude: all tested nMe are highly flammable, all nonpassivated nMe can ignite on contact with air in critical environments, nAl and nZn react with water releasing hydrogen, nFe is pyrophoric.

Solid rocket propellants are intrinsically sensitive to a variety of external stimuli. Incorporating nMe powders increases the level of risks associated with the life cycle of the loaded formulations. Hazardous properties can only be evaluated by experimental testing including impact, friction, card gap, critical diameter, spark, ESD, and so on. Aluminum powders, either micron-sized or nano-sized, are in general insensitive to friction and impact. Solid propellants

loaded with  $\mu\text{Al}$  powder are, in general, little sensitive to friction and impact. But replacement of  $\mu\text{Al}$  with  $\text{nAl}$  yields a significant increase in solid propellant safety hazards.

Regarding mechanical hazards, for the tested AP/HTPB-based composite propellants [24-25], use of  $\text{nAl}$  instead of  $\mu\text{Al}$  implies a moderate increase in friction sensitivity and less increase in impact sensitivity. While all tested  $\text{nMe}$  and  $\text{nMeO}$  in general increase the hazard level,  $\text{Al/Fe}_2\text{O}_3$  nanocomposite [41] brought no change in friction sensitivity of propellant samples. The presence of  $\text{nZr}$  and  $\text{RDX}$  revealed most dangerous when added to AP/HTPB formulations [24-25]. The fuel rich  $\text{Al/PTFE}$  particles revealed safe threshold values for ESD, impact, and friction ignition [37].

Regarding ESD, the average energy that a human body can deliver is 15 [4] to 78 mJ [44]. In either case, it is enough to ignite  $\text{nMe}$  powders:  $\text{nAl}$  requires 1 to 12 mJ [4], while  $\mu\text{Al}$  needs about 400 mJ. Thus, equipments should be electrically grounded and only electrically nonconductive material should be used for containers and handling of  $\text{nAl}$ . In general, results for ESD threshold are less readily available for solid propellants. ESD sensitivity of  $\text{nMe}$ , and that of mixes containing  $\text{nME}$ , may be much higher than the ESD of micron-size powders [44]. In particular,  $\text{nAl}$  sensitizes  $\text{ADN}$ ,  $\text{AP}$ , and  $\text{RDX}$ ; but this negative effect can be mitigated by particle coatings, such as  $\text{PE}$  (PolyEthylene) and  $\text{PP}$  (PolyPropylene) for  $\text{ADN}$  and  $\text{AP}$ .

## AGING

Aging is a critical issue regarding the use of nanoenergetic ingredients. For all applications, the mechanical and chemical integrity as well as ballistic performance of the aging solid propellant grains should be maintained as manufactured. This is not an easy task, being any solid propellant formulation a living chemical organism with on-going slow rate reactions possibly promoted by the environmental conditions ( $\text{O}_2$ , humidity, temperature, vibrations). During aging, a propellant undergoes different degradation processes that irreversibly change it. The amount of degradation depends on several processes of chemical, physical, and mechanical nature.

Chemical and physical processes are related to molecular reactions and diffusion phenomena, which are governed by kinetic processes and can be accelerated by increasing the temperature. To simulate the long-term aging within a reasonable time period, propellant samples are aged at temperatures higher than ambient temperature. This allows predicting the material behavior with data obtained in shorter experimental times, but it assumes that the chemi-

cal processes are identical with those occurring under the natural aging. Unfortunately, this assumption is not always fulfilled.

The shelf life of pristine nAl is too short for propulsive applications. But it can significantly be extended by proper coating: palmitic or stearic acid, PE or PP in [44], organic silanes, HTPB in [4][43]. Another approach is surface passivation, as discussed next.

### PASSIVATION

Differently from the conventional  $\mu$ Al, the surface of nAl particles is in general very reactive and even pyrophoric in air. Stabilization through passivation (surface-modification) of nAl particles is mandatory to avoid spontaneous ignition in air, useful to control reactivity, and a promising technique to extend the shelf life of nAl during storage. For EEW produced powders, the details of the process are important. For example, the minimum thickness of oxide-hydroxide protective layer is formed for nAl produced in  $H_2$ .

Many nAl samples were produced by EEW in Ar,  $N_2$  or ( $N_2 + CO_2$ ) environments [30]. Powders were passivated by coating films of gas ( $N_2$ ,  $CO_2$ , and air), of liquid in a solvent (NC, oleic acid  $C_{17}H_{33}COOH$ , and stearic acid  $C_{17}H_{35}COOH$  suspended in kerosene or ethanol), of liquid without a solvent (fluoropolymer), and of solid (boron and nickel). Based on four common parameters (Al oxidation enthalpy,  $Al \rightarrow Al_2O_3$  fractional degree of conversion, specific surface area  $S_{sp}$ , and metal content  $C_{Al}$ ), best results were achieved in the samples dry-passivated by boron, air and  $CO_2$ . The reference Alex in air had  $C_{Al}$  was 86% at start and decreased to 85% after 12 months storage at room temperature and 70% RH (relative humidity). The best nAl sample was produced in Ar + 10 vol %  $H_2$  and passivated in air, featuring a  $C_{Al}$  was 92% stable over the 12-month test period [30]. Stearic acid, and especially oleic acid, both interacted with Al and depleted the metal content: in the case of oleic acid, passivation decreased  $C_{Al}$  to 45% at start and went on to 43% after 12 months.

### CONCLUDING REMARKS

Modest reproducibility and difficult control of nanoingredient properties make, in general, difficult their use at industrial level and hazardous any extrapolations at scientific level. Yet, the very wide and diversified experimental testing conducted all over the world with an array of nanopowders and nanocomposites shows faster burning rates, quicker ignition, a reduction of incipient agglomeration phenomena, and an array of new burning effects.

However, for the currently used materials, there is no extra energy in using nano-sized ingredients instead of the corresponding micron-sized versions. Therefore, not a gain but actually a drop in the ideal specific impulse can be expected for rocket propulsion. Some recovery is in principle possible for the delivered specific impulse by enough squeezing of the performance losses intrinsically associated with micron-sized energetic ingredients. Most important are the 2P flow losses associated with the supersonic gasdynamic nozzle. It is true that aggregates/agglomerates of smaller sizes are produced by nAl at the burning surface, but their final fate after expansion through a gasdynamic nozzle is not clear. Even if the 2P losses are mitigated, use of nAl also implies several negative effects. Loss of active metal, clustering during manufacture and storage, EOM viscosity, possible impairment of mechanical properties, less effective acoustic damping, aging, and cost (even though it is nowadays much diminished) are more than enough to balance the expected advantages. Moreover, with increasing nAl fraction, friction sensitivity, impact sensitivity, but also the measured heat of combustion (because of higher combustion efficiency), all increase [24-25]. As of today, no propulsive system at industrial level uses nanoenergetic ingredients.

Among the many alternative ways to replace the conventional  $\mu$ Al in solid rocket propulsion, nAl is the one most prone to loss of active Al content. An additional, subtle way for nEM in general to fail is due to clustering phenomena. During propellant manufacture and storage, nanoparticles form “grape bunches” due to the electric charge accumulated on the particle surface and the greater surface energy. The result of this process of aggregation of small particles is the formation of large clots of ultrafine particles with 0.3–0.6  $\mu$ m diameter. Different mitigation strategies have been attempted, from ultrasounds to colloidal dispersion and from mixer velocity to particle coatings [4], but no decisive progress has been realized. Clustering of nanoparticles, slurry viscosity, propellant density, and propellant mechanical properties are all intermingled. Moreover, possible local spots featuring high Al concentration may react with fast heat release rate and induce non-uniform combustion over the burning surface.

Thus, the dispersion quality of the nEM is of paramount importance. In this respect, a fundamental doubt was underlined by Zachariah et al. [5]. Reactive molecular dynamics simulations of a couple of oxide coated nAl particles showed that in general, for aggregates of nAl, sintering into larger structures can occur on time scales faster or comparable to combustion reaction. Should this happen prior to significant combustion, the material will exhibit the kinetics of larger particles and lose the original nanostructure during condensed phase reactions.

Within the current rocket propulsion technology, ultrafine particles in the range, say 50 to 150 nm, are preferable to true nano-sized particles. Maybe this will change in the future, but not in the short term. Steady burning rates strongly increase by decreasing size particles over the explored nanometric range, but for very small particles the appreciable decrease of  $C_{Al}$  makes useless a further increase; see Fig.3. Pressure exponents show only minor changes under standard operating conditions for the AP/HTPB workhorse formulations, but may considerably vary for wider changes of the tested formulations and enforced operating conditions. Also, an appreciable decrease is found for ignition of nAl particles in the range 100–200 nm.

In rocket propulsion, so far nEM has been more useful for basic understanding and laboratory investigations than real world system applications. Augmentation of steady burning rates, quicker ignition, and maybe less agglomeration are of general interest but with only mild effects on the well-behaved propellant formulations used for space exploration. More substantial effects can be achieved for “off-design” or unusual operations such as plateau burning, self-sustained oscillatory burning, PDL,  $dp/dt$ , ignition, large changes of pressure exponent, and more. At the time of writing, one can safely recommend only the addition of small fraction of nAl to improve and/or fine tailor ballistic properties or for very specific tasks, such as reduced smoke exhausts. Minor replacements (10-20%) by nAl out of the total Al load can be very effective for steady burning rate augmentation and incipient agglomeration reduction.

As to future work, open problems concern technological matters such as coating selection and control, uniform dispersion, handling and storage safety. More penetrating questions regard understanding of flame structure, ignition trigger, and aging mechanism. Fundamental doubts involve the behavior of monomolecular high-energy materials: why AP and RDX increase their self-deflagration rates by decreasing particle size whereas ADN and HMX seem to behave the opposite way.

In conclusion, we have only begun to scratch the surface of research in the nanoworld. Performance enhancements as well as novel modes of operation are potentially within reach. But the practicality of nanotechnology is yet questionable. When large-scale use of nanomaterials in rocket propulsion will become practical depends on such factors as cost, unproven long-term stability, and handling/safety issues.

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