

Effects of Nano-Sized Al on the Combustion Performance of Fuel Rich Solid Rocket Propellants

W.Q. Pang^{1*}, F.Q. Zhao¹, L.T. DeLuca², C. Kappenstein³, H.X. Xu¹, X.Z. Fan¹

¹ Xi'an Modern Chemistry Research Institute, Xi'an P.R.China 710065

²Space Propulsion Laboratory, Aerospace Science and Technology, Politecnico di Milano, Italy I-21056

³Institute of Chemistry of Mediums and Materials of Poitiers, University of Poitiers, F-86073 Poitier, France

Article info

Received:
8 January 2016

Received and revised form:
12 March 2016

Accepted:
24 April 2016

Keywords:

physical chemistry,
fuel rich solid propellant,
nano-sized Al powder,
combustion property

Abstract

Several industrial- and research – type fuel rich solid rocket propellants containing nano-metric aluminum metal particles, featuring the same nominal composition, were prepared and experimentally analyzed. The effects of nano-sized aluminum (nAl) on the rheological properties of metal/HTPB slurries and fuel rich solid propellant slurries were investigated. The energetic properties (heat of combustion and density) and the hazardous properties (impact sensitivity and friction sensitivity) of propellants prepared were analyzed and the properties mentioned above compared to those of a conventional aluminized (micro-Al, mAl) propellant. The strand burning rate and the associated combustion flame structure of propellants were also determined. The results show that nAl powder is nearly “round” or “ellipse” shaped, which is different from the tested micrometric Al used as a reference metal fuel. Two kinds of Al (nAl and mAl) powder can be dispersed in HTPB binder sufficiently. The density of propellant decreases with increasing mass fraction of nAl powder; the measured heat of combustion, friction sensitivity, and impact sensitivity of propellants increase with increasing mass fraction of nAl powder in the formulation. The burning rates of fuel rich propellant increase with increasing pressure, and the burning rate of the propellant loaded with 20% mass fraction of nAl powder increases 77.2% at 1 MPa, the pressure exponent of propellant increase a little with increasing mass fraction of nAl powder in the explored pressure ranges.

Nomenclature

Al	aluminum powder
AP	ammonium perchlorate
HTPB	hydroxy-terminated polybutadiene
DOS	di-2-ethylhexyl sebacate
mAl	micro-sized aluminum powder
nAl	nano-metric aluminum powder
SEM	scanning electron microscopy
Width	$(d_{90}-d_{10})/d_{50}$
TDI	2,4-toluene diisocyanate
d_{10}	particle diameter corresponding to 10% of the cumulative under size distribution, μm
d_{50}	median particle diameter, μm
d_{90}	particle diameter corresponding to 90% of the cumulative under size distribution, μm
r	strand burning rate, $\text{mm}\cdot\text{s}^{-1}$
a	pre-exponential factor of burning-rate law
ρ	density, $\text{g}\cdot\text{cm}^{-3}$
n	pressure exponent
p	pressure, MPa
τ	yield stress, MPa
η	viscosity, $\text{Pa}\cdot\text{s}$

1. Introduction

The specific impulse of solid propellants can be increased by the addition of certain reactive metal powders such as aluminum, magnesium, and boron powder, et al. These metal fuels mentioned above are excellent additives with the most potential, in terms of gravimetric or volumetric enthalpy release and density [1–3]. These metals can increase the energetic properties for solid rocket propellants, thus, they are frequently used to augment performance of solid and hybrid rockets [4–7]. Metal powders, in particular aluminum, are used as energetic fuels in composite solid rocket formulations with the purpose of increasing ballistic motor performance. However, during combustion, aluminum undergoes a series of complex chemo-physical phenomena leading to the formation of condensed combustion products (CCPs) under a variety of shapes and sizes. This in turn yields partial combustion and slag

* Corresponding author. E-mail: nwpu_pwq@163.com

formation in the combustion chamber, throat erosion and two – phase flow losses in the supersonic nozzle, and thus ultimately perceivable losses of the delivered specific impulse. Investigations have been carried out all around the world during the last few decades, to improve the delivered performance of the AP/Al/HTPB compositions with metal powder used for space launchers [8–11]. Effect on the primary combustion performance of aluminum particle sizes in fuel rich propellant with high aluminum content was studied. The results show that the presence of UFAl (ultra – fine aluminum) improves the combustion performance of propellants. The heat from the gas phase reaction could be increased because more and more UFAl can take part in the gas phase reaction due to its small particle size [12–14]. Significant increases in propellant burning rates, shorter ignition delays, and shorter agglomerate burning times were recently obtained for composite solid propellant formulations containing ultra – fine energetic particles, particularly nano-Al particles [15–18]. Chemical composition and grain size distribution strongly affect the physicochemical properties and morphology of the residues. And much attention was dedicated to understand phenomena occurring at and/or near the combustion surface where agglomeration phenomena dominate. The burning rate of propellant is affected by changes in composition (ingredients, mass fraction), particle size and particle size distribution, and operating conditions (pressure and initial temperature). Experimentalists and modelers vary these factors to determine their influence on burning rate as well as other properties in order to find the best composition for a given application.

Although so many achievements in the experimental study of metalized fuels systems have been made [19–23], with renewed interest in energetic metals, many fundamental issues concerning the effects that the actual particle size has on the ignition and combustion characteristics, when used as components of solid rocket propellants, remain to be clarified. In addition, only few data are available on the effects of metal particle and grain size on the combustion features of propellants, specifically mechanical sensitivity, and burning rate character-

istics of the fuel rich solid propellants containing different aluminum particles sizes. So in our study, the characteristics of different kinds of Al powders were analyzed by using SEM and laser granulometry diagnostic techniques. In order to compare the performances of nAl and mAl powder, as well as possible synergies between the metal fuels, two more Mg/Al-based fuel rich propellants containing different mass fractions of the same nAl metal powder were manufactured. Emphasis is placed on investigating combustion properties (burning rate and pressure exponent) and mechanical sensitivity of propellant samples, which could be useable for ram jet application.

2. Experimental

2.1 Materials and specimen

Hydroxy terminated polybutadiene (HTPB, $E_{OH} = 7.8 \times 10^{-4}$ mol/g) cured with 2,4-toluene diisocyanate (TDI), di-2-ethylhexyl sebacate (DOS, $\geq 99.4\%$), mAl powder (Al-1, 5 μm , $\geq 99.8\%$) and nAl particles (Al-2, $d_{50} = 50$ nm) were used as components of composite solid rocket propellant. Bimodal distributions of ammonium perchlorate (AP) were utilized in the propellant formulation. The first mode consisted of pure research grade ($> 99\%$ pure) ammonium perchlorate with an average particle size of 0.105–0.147 μm . The second AP mode was made by grinding ammonium perchlorate ($> 99\%$ pure) in a fluid energy mill to an average particle size of around 1–5 μm . Except where otherwise stated, all propellants were manufactured, processed, and tested at Xi'an Modern Chemistry Research Institute under identical conditions and using identical procedures.

Table 1 shows the percentages by mass of these chemicals in four different propellant formulations.

Propellant formulations were mixed in 500 g batches using a 2 L vertical planetary mixer. All samples were prepared by slurry cast technique at the temperature of 35 °C and then solidified for 96 h (50 °C) in a water jacketed oven. All samples were successively machined to a fixed dimension (shape: length: 100–150 mm; width: 2–5 cm, height: 2–5 cm).

Table 1

The mass fractions of main ingredients for composite solid propellant

Samples	HTPB/%	Al-1/%	nAl/%	Mg/%	AP/%	Additives/%
NA-1 (Reference formulation)	22	20	-	21	35	2
NA-2	22	15	5	21	35	2
NA-3	22	10	10	21	35	2
NA-4	22	-	20	21	35	2

2.2 Equipment and experimentation

2.2.1 SEM and particle size distribution experiments

Scanning electron microscopy was used to study the shape, size, morphology and defects of powders. The morphology of metal particles was examined by SEM technology. Granulometric analyses (particle size, particle size distribution and specific surface area) of samples were performed through laser scattering (Malvern Mastersizer 2000) using a dry dispersion unit. The quantity of material per test was about 0.07 to 0.10 g. Obscuration filtering was switched on and set to values within the range of 0.5–10%.

2.2.2 Rheological experiment

Different metal particles were mixed with HTPB binder in the mass ratio of 1/1. The viscosity of the propellant slurry was determined using a HAAKE cylindrical rotational rheometer RS 300. The samples were tested in the coaxial cylinder sensor system at a temperature of about 50 °C.

2.2.3 Heat of combustion test

The theoretical heat of combustion was obtained by using “Ideal Gauss Law”. It was calculated according to equation (1) as follows

$$H_u = x_1 H_{u1} + x_2 H_{u2} + \dots + x_n H_{un} \quad (1)$$

where H_u is theoretical heat of combustion, J/g; x_1 is mass fraction of the first ingredient; H_{u1} is theoretical heat of combustion the first ingredient, J/g; x_2 is mass fraction of the second ingredient; H_{u2} is theoretical heat of combustion the second ingredient, J/g; x_n is mass fraction of the n ingredient; H_{un} is theoretical heat of combustion the n ingredient, J/g.

The measured heat of combustion values can be investigated by means of an isothermal method. A definite mass of propellant sample was put into the calorimetric oxygen bomb, which is surrounded by a fixed mass of water. The propellant was ignited in the bomb, the heat of explosion of the sample was calculated according to equation (2) after the values of the water temperature increases were measured.

$$Q_v = (C\Delta T - q_1)/m \quad (2)$$

where Q_v is heat of explosion, J/g; C is thermal capacity of the calorimeter, J/K; ΔT is the measured temperature increase during combustion, K; q_1 is heat of explosion of initiation wire, joule (J); m is mass of sample, gram (g).

2.2.4 Density test

The density measurement of propellants was carried out on a Model AG 104 METTLER TOLEDO balance with the rectangular shaped of 30 mm × 30 mm × 10 mm, which were steeped in the medium of liquid paraffin at the temperature of (20 ± 2) °C.

2.2.5 Hazardous properties test

The hazardous properties of the propellant compositions to impact stimuli were determined by applying the fall hammer method (2 kg drop weight) in a Bruceton staircase apparatus [24] and results were given in terms of statically obtained 50 % probability of explosion (H_{50}). Friction sensitivity was measured on a Julius Peter apparatus [25] by incrementally increasing the load from 0.2 to 36 kg, until no ignition was noted in five consecutive test samples.

2.2.6 Burning rate test

A metal fine wire (0.1 mm in diameter) was threaded through the top of the strand with a alternate voltage of 100 V to ignite the propellant strands (diameter = 5–6 mm, length = 140 mm) at an initial temperature of 20 °C. The samples were placed vertically on the combustion rack and a sealed combustion chamber filled with a nitrogen atmosphere.

The burning rate measurements of propellant samples are realized as follows: when a propellant strand is ignited under the nitrogen gas purge conditions, the pressure in the strand burner increases due to the addition of the gaseous products. However, the pressure valve attached to the nitrogen gas supplier is regulated automatically to reduce the nitrogen gas flow rate in order to maintain the pressure constant. Thus, the pressure in the burner is maintained at the desired pressure. Burning rate is measured by determining the instant of melting of each of 5 low-melting-point fuse wires of lead metal, 5 mm in diameter, threaded through the strand at accurately known separation distances (140 mm). These 5 fuse wires, each in series with a resistor, form 5 parallel arms of an electrical circuit, whose output voltage changes discontinuously as soon as a fuse wire melts. The temperature of the strand can also be measured by a calibrated copper-constantan thermocouple threaded through the strand with the bead of the thermocouple is placed in the center of the strand. The real time data is recorded by a computer which processes and calculates the burning rate. Five replicate experiments are conducted at each test pressure and the average experimental results are obtained with the relative standard deviation of 0.13–0.25.

3. Results and Discussion

3.1. SEM and grain size distribution analysis

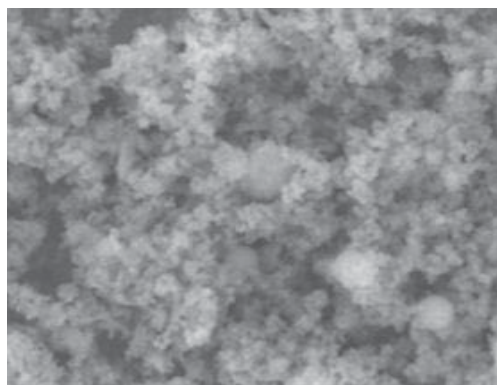
Detailed morphology information concerning the powder was collected by running a series of advanced diagnostic techniques, including scanning electron microscope (SEM) and grain size distribution. The well-dried aluminum particles were free of fluid, the microstructures and grain size distribution results are shown in Fig. 1 and Table 1, respectively.

It can be seen from Fig. 2 and Table 2 that the microstructures of the two different kinds of tested Al powders present various shapes. The nano-sized Al powder is nearly “round” or “ellipse” in shape, which is different from the tested micrometric Al used as a reference metal fuel. There is a serious particle clustering, which the smaller sized particles adsorb on the surface of bigger ones, and the space interactions between the particles are much significant. The median diameters d_{50} of nAl is 49.3 nm, which is much lower than that of the micrometric one. Corresponding to the lower values of d_{50} , the specific surface area of tested nAl powder is $55.080 \text{ m}^2 \cdot \text{g}^{-1}$, which is much larger than that of the micrometric one ($1.321 \text{ m}^2 \cdot \text{g}^{-1}$). While the width of nAl particles is 1.154, which is a bit lower than that of the micrometric aluminum particles (2.857).

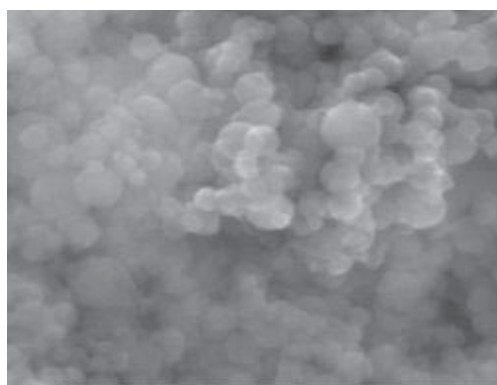
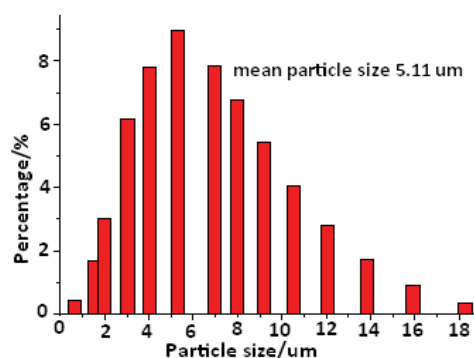
3.2 Effects of nAl mass fraction on the rheological property of propellant slurry

Nanometric particles, for their much larger specific surface area have a significant influence to the rheological properties of propellants. The effects of nAl powder mass fraction on the rheological properties of solid propellants slurry are shown in Fig. 2.

It can be seen that the yield stress and viscosity of Al-based fuel rich propellant slurry increase with increasing mass fraction of nAl powder. From the perspective of macro flowing view point, the flowing properties of slurry become worse, and the pot life becomes shorter, especially when 10% mass fraction of nAl added to the formulation. In this case, the static friction resistant interactions increase among the solid fillers, and the physical cross-link between nAl and HTPB augment. Moreover, for the slurry containing 20% mass fraction of nAl powder, the viscosity get up to $2000 \text{ Pa} \cdot \text{s}$ in 2 h, which can no longer flow. Its pot life is less than 2 h, whereas, the pot life of fuel rich propellant loaded with micrometric Al powder is more than 5 h. This phenomenon can be attributed to the large specific surface area, morphology and particle size distribution characteristics of nAl powder. An additional point worth to be noted is that there is one peak point in the rheological curve of propellant loaded with 5% up to 10% mass fraction of nAl powder.



(a) Al-1: Micro-sized Al particles



(b) Al-2: Nano-sized Al particles

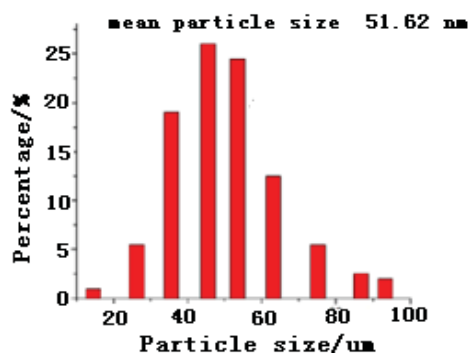


Fig. 1. SEM images and grain size distribution of tested aluminum particles.

Table 2
The characteristics of different aluminum particles

Items	unit	Al-1	Al-2
d_{10}	μm	1.012	0.018
d_{50}	μm	5.078	0.049
d_{90}	μm	15.51	0.094
Width	-	2.857	1.544
Density	$\text{kg}\cdot\text{m}^{-3}, \times 10^3$	2.70	2.70
Mass heat of combustion ^{a)}	$\text{MJ}\cdot\text{kg}^{-1}$	31.02	31.02
Vol. heat of combustion ^{b)}	$\text{kJ}\cdot\text{cm}^{-3}$	83.75	83.75
Relative atomic mass	-	26.98	26.98
Melting point	$^{\circ}\text{C}$	660	660
Boiling point	$^{\circ}\text{C}$	2447	2447
Specific surface area	$\text{m}^2\cdot\text{g}^{-1}$	1.32	55.08

Note: ^{a)} and ^{b)} are neat aluminum powder, the alumina shell is not considered.

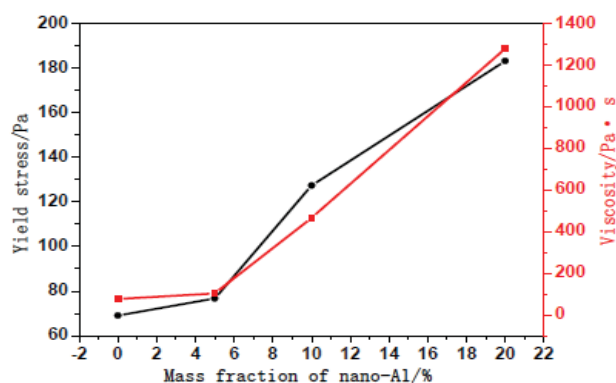


Fig. 2. Effect of different mass fraction of nAl on the rheological property of fuel rich solid propellants.

The increasing yield stress of fuel rich propellant slurry loaded with nAl powder can be attributed to the interspaces among nAl powders which adsorb large amounts of liquid ingredient, which in turn decrease the relative distance of solid fillers, and increase the static friction interaction etc, between solid particles. Moreover, the resistant interactions between fillers and polymer binder increase, and

the relative liquid ingredients reduce with increasing mass fraction of nAl powder in the formulation. It was found [26] that the viscosity of propellant slurry reflects its inner friction in the flowing state, and the inner friction can be controlled by HTPB pre-polymer. nAl powder, for its large specific surface area, is easy to cluster, it adsorbs part of HTPB strain, and restricts the movement of HTPB molecule chain, which in turn leads to increasing HTPB molecular weight and flowing resistance. With increasing mass fraction of nAl powder, the physical cross-link point increases, which results in a viscosity increase of propellant slurry.

3.3 Properties of fuel rich propellants

3.3.1 Energetic properties (density and heat of combustion)

The densities and heat of combustion measurements were conducted for each propellant and were compared with the theoretical data. Table 3 summarizes the results of these tests, as measured at our Institute.

Table 3
Effects of different mass fraction of nAl powder on the energetic properties of fuel rich solid propellants

Samples	nAl /%	Density/ $\text{g}\cdot\text{cm}^{-3}$	Heat of combustion/ $\text{MJ}\cdot\text{kg}^{-1}$		Combustion efficiency/%
			Theoretical data	Measured data	
NA-1	0	1.641	23.120	21.637	93.60
NA-2	5	1.636	23.120	22.251	96.24
NA-3	10	1.632	23.120	22.544	97.51
NA-4	20	1.627	23.120	22.795	98.59

It can be seen from the results in Table 3 that the density of fuel rich solid rocket propellants with different mass fraction of nAl particles is in the range of 1.627–1.636 g·cm⁻³, which is lower than that of the propellant with micrometric Al powder (1.641 g·cm⁻³). The decreased density of propellant with increasing mass fraction of nAl powder in the formulation can be attributed to the percentage raise of high density materials, thus leading to an increase in propellant density, and the modest porosity of nAl powders during the manufacture of propellant formulation.

The measured heat of combustion of fuel rich propellant increases a little when a given mass fraction of micrometric Al is replaced by nAl powder in the formulation. Moreover, the values of the measured heat of combustion are lower than the theoretical ones, and this effect can be ascribed to the different combustion efficiency of micrometric Al and nanometric Al powder in the solid composites. Thus, the combustion efficiency of nAl powder in some degree is higher than that of the micrometric one.

3.3.2 Hazardous properties

Nano-sized metal particles have much influence on the impact and friction sensitivity of solid propellants. Thus, it is necessary to study the hazardous properties of fuel rich propellants with and without nAl particles. Results of the hazardous properties experiments are shown in Fig. 3.

It can be seen from the results in Fig. 3 that the friction sensitivity and impact sensitivity of fuel rich propellant increase with increasing mass fraction of nAl powder. The slope of increasing propellant friction with nAl powder is much higher in the mass fraction range of 0–5% than in the remaining interval, while the impact sensitivity of propellant decreases significantly when nAl powder is in the mass fraction range of 5–20%. The increase of mechanical sensitivity of propellant can be attributed to the large specific surface area of nAl powder and the active Al content on the surface of Al powder [2, 8, 10–12]. Compared to micrometric Al powder, a large number of spaces exist between the micro – particles for its large specific surface area during the process of particles, such as friction or impact. The air absorbed in the space come into “hot spot” when compressed, and the increasing temperature of the “hot spot” urge the decomposition of condensed AP and the condensed reaction between AP with nAl powder, until finally deflagration occurs.

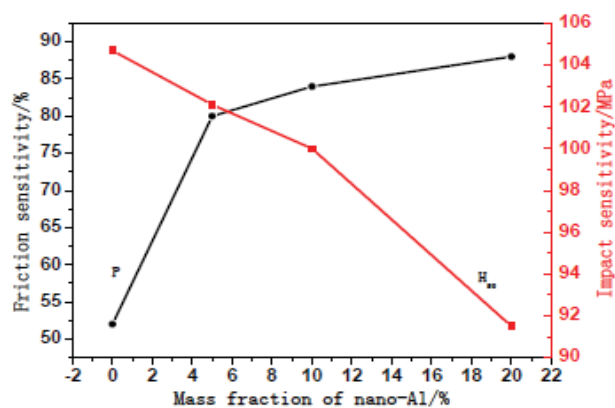


Fig. 3. Effect of different mass fraction of nano-Al on the mechanical sensitivity of propellants.

3.4 Effects of nAl particles on the combustion properties of fuel rich propellants

3.4.1 Burning rate and pressure exponent

Propellant burning rates determine the rate of gas generation, which determines the pressure inside the motor and the overall thrust. Burning rates herein are obtained experimentally by burning small propellant strands and measuring the surface regression versus time. Literature on combustion of metal particles indicates that ignition could probably take place via two potential pathways [17–21]. One is the destruction of the metal oxide layer due to cracking, and the other is self-heating due to oxidizer diffusion through the oxide layer, and hence melting of the layer. Various factors like the particle diameter, oxidizing species, pressure, and temperature affect the burning rate of the particles.

The burning rate data of the propellants with and without nAl particles obtained under different pressures are shown in Table 4 and Fig. 4.

It can be seen in Fig. 4 that different mass fraction of nAl additives can affect the combustion behavior and change the burning rate of fuel rich propellant for the same total amount of Al, keeping the remaining composition unaltered. The burning rates of solid fuel rich propellant increase with increasing pressure, and the increase extent in the pressure range of 0.5–1 MPa is obviously higher than that in the pressure range of 2–3 MPa for all the formulations. Although the Mg/Al-based fuel rich formulation containing micrometric Al powder exhibits a low burning rate, a partial replacement with nAl particles may boost the burning rate higher than that of the micrometric Al powder formulation. The burning rate increases by 77.2% for fuel rich propellant loaded with 20% mass fraction of nAl powder at 1 MPa. Moreover, the propellant pressure exponent increases a little for increasing

mass fraction of nAl powder in the explored pressure range, and the pressure exponent of NA-1 formulation is 0.38 (0.5–3 MPa), which is the lowest one compared to those of the others. The nAl powders have small size effects, their promoting effect on the combustion of propellant being the main function in the low pressure range. The specific performance is as follows [26–28]: (1) the burning rate of nAl powder itself is higher than that of micrometric Al powder; (2) the ignition threshold of nAl is lower than that of micrometric Al powder, and the value increases with an increase in particle size; (3) from the view of heat transfer, the addition of nAl powder in the propellant can effectively increase the adsorption heat in the combustion process. From the view of dynamics, nAl powder can contact polymer binder and gaseous reactants because of their large specific surface area. Also, the heat release and heat transmission at the combustion surface for nAl are higher than the values for micrometric ones at high pressure range.

As we know, moderate nAl can increase the burning rate of composite solid propellant in a large pressure range [29, 30]. This is because the ignition temperature of nAl is lower and reactive activity is higher than that of micrometric one. On the

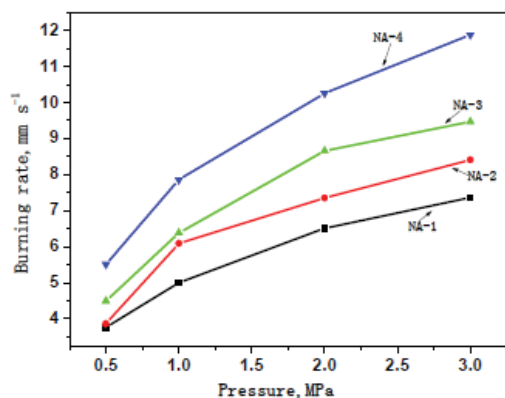
one hand, the lower ignition temperature can make nAl powder oxidized and release heat in the low temperature range about 500–600 °C. This implied a large heat feedback to the combustion surface, which can improve the combustion performance of solid propellants, and increase the burning rate of propellant. On the other hand, the higher reactivity of nAl can shorten the ignition delay and combustion time, there is little condensed combustion product and much heat release feedback to the burning surface of propellant. For Mg/Al-based fuel rich propellants, the slope of increase of burning rate is a bit low, which may be related to the lower mass fraction of oxidizers in the formulation. There is not enough oxygen to oxidize nAl and other fuels in this fuel rich system, and the potential energy of high-energy fuels cannot be fully released.

3.4.2 Combustion flame structures

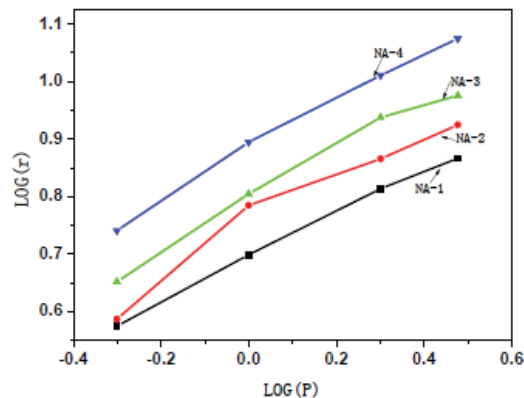
In order to know the effects of nAl particles on the combustion flame structure of Mg/Al-based fuel rich solid rocket propellants, the combustion flame structures of fuel rich propellants with different mass fraction of nAl particles at 1 MPa are shown in Fig. 5.

Table 4
Effect of nAl on the combustion characteristic of propellants

Samples	nAl /%	$r/\text{mm}\cdot\text{s}^{-1}$				$n(0.5\text{--}3\text{MPa})$
		0.5 MPa	1 MPa	2 MPa	3 MPa	
NA-1	0	3.76	5.01	6.51	7.36	0.38
NA-2	5	3.86	6.09	7.35	8.41	0.42
NA-3	10	4.49	6.38	8.66	9.47	0.43
NA-4	20	5.51	7.86	10.26	11.8	0.43



(a) Pressure – Burning rate



(b) $\log(P)$ – $\log(r)$

Fig. 4. Burning rate of fuel rich solid propellant with different mass fraction of nano-sized Al particles at different pressures (pressure range: 0.5–3 MPa; initial temperature: $T_0 = 293$ K).

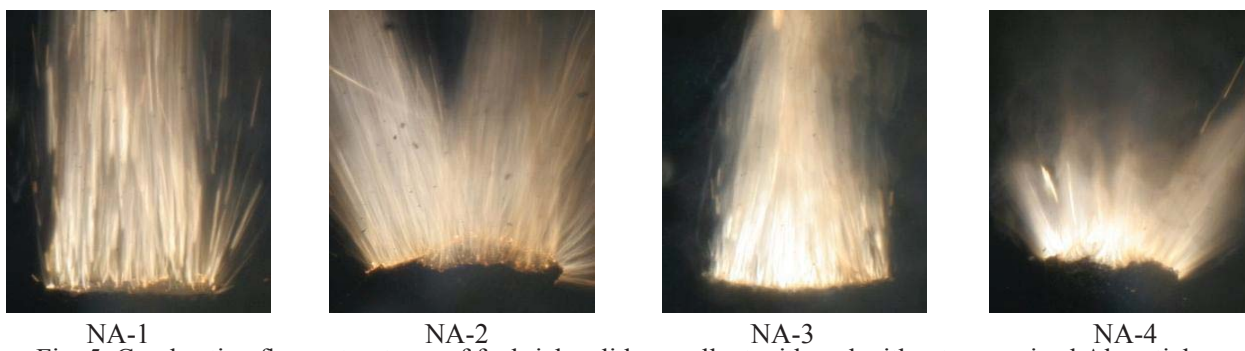


Fig. 5. Combustion flame structures of fuel rich solid propellant with and without nano-sized Al particles.

From the results of Fig. 5, it can be seen that the combustion flame structures of fuel rich propellants with and without nAl particles present multi-flame structures. There are many sparks on the propellant surface during the combustion process, which can be attributed to the addition of metal particles in the propellant formulations. Although the metal oxidation process follows a common set of events, aggregation/agglomeration phenomena near the burning surface are noticeably different depending on the enforced operating conditions and details of the propellant formulation. The incipient agglomeration for nAl powders is smaller than for common Al powders, and the luminosity of combustion flame structures for propellant containing nAl particles is magnified, which may be attributed to the small size of nAl powder in the compositions.

3.4.3 Combustion flame residues analysis

In the combustion of Mg/Al fuel rich propellants, in general, the primary combustion temperature is low (at about 2000 K), Al almost cannot burn at this temperature, and most part of the Al load is just heated and melt, then pushed into the second combustion chamber. The addition of nAl

to the propellant composition can increase reactivity and make burning to occur more fully. In order to compare the reaction completeness of nAl in fuel rich propellants, the combustion residues were collected at 1 MPa, and the crystallized component and mass content of combustion products were analyzed by using X-ray diffraction method. The results are shown in Table 5.

It can be seen that the detected residual content of Al decreases with increasing mass fraction of nAl in the composition. There is no Al detection when all micrometric Al is replaced by nAl in the propellant. The addition of nAl powder to the formulation can improve the primary combustion and reaction degree, which in turn increase heat release and temperature of products. Overall, this process has the advantage to improve the secondary combustion efficiency.

In order to investigate the effect of nAl on the energetic and combustion properties of Mg/Al – based fuel rich propellants loaded with nAl powder, the mass fraction of micrometric Al and nAl were calculated and investigated by using X-ray fluorescence method. To explain the improvement of nAl to the heat of combustion of fuel rich propellants, also the active Al content was calculated. The data are shown in Table 6.

Table 5
The main products composition of combustion residues

Samples	nAl/%	MgO	Al	Mg ₂ (OH)ClCO ₃ ·3H ₂ O	MgAl ₂ O	Al ₄ C ₃	Al ₂ O ₃	AlOCl
NA-1	0	38.69	14.60	29.61	9.15	7.95	0	0
NA-2	5	37.73	12.04	29.53	13.21	7.49	0	0
NA-3	10	25.59	7.42	25.87	22.62	11.00	7.50	0
NA-4	20	27.46	0	0	35.47	0	19.42	17.65

Table 6
The main composition of the two types of aluminum powder

Samples	W/%					Pure Al/%
	Al	O	Si	Mg	Fe	
Al (5 um)	97.5	2.16	0.196	0	0.112	95.06
nAl	84.9	13.0	0	1.90	0	79.8

It can be seen from the data in Table 6 that the mass percentage of elemental O in nAl powder is much higher than that of micro-Al powder, which indicates that the nAl powder is more efficiently oxidized for its large specific surface area. The active Al content of micro-Al powder (95.06%) is much higher than that of nAl powder (73.8%). The theoretical heat of combustion decreases with increasing mass fraction of nAl powders (including alumina) in the formulation. The measured heat of combustion increases after subtracting the impurity alumina on the surface of Al particle, which indicate that nAl can be combusted fully. There is much heat release for nAl powder, and its combustion efficiency is higher than that of micrometric ones.

4. Conclusions

(1) Nano-sized Al powder displays a nearly “round” or “ellipse” shape, which is different from the tested micrometric Al used as a reference metal fuel.

(2) The density of propellant decreases with increasing mass fraction of nAl powder, the measured heat of combustion, friction sensitivity, and impact sensitivity of propellants all increase with increasing mass fraction of nAl powder in the formulation.

(3) The burning rate of the propellant loaded with 20% mass fraction of nAl powder increases by 77.2% at 1 MPa, while the pressure exponent of propellant increases a little with increasing mass fraction of nAl powder in the investigated pressure range.

Acknowledges

This paper was supported by the Science and Technology Administration of National Defense Metrology Project (JSJL2014208A007). The authors wish to thank Xie QiuLian, Cao FangJie and Wang Ying, The Analyzed Measuremental Center, Xi'an Modern Chemistry Research Institute for carrying out scanning electron microscope (SEM), particle size distribution, hazardous properties and combustion structure analyses of the tested experiments, Xi'an Modern Chemistry Research Institute for useful suggestions in assessing the statistical data collection errors.

References

- [1]. Richard A. Yetter, Grant A. Risha, *Proc. Combust. Inst.* 32 (2009) 1819–1838.
- [2]. David E.G. Jones, Richard Turcotte, Robert C. Fouchard, Queenie S.M. Kwok, Anne-Marie Turcotte, and Zainab Abdel-Qader, *Propellants, Explos. Pyrotech.* 38 (2013) 852–859.
- [3]. Weiqiang Pang, Xuezhong Fan, Fengqi Zhao, Huixiang Xu, Wei Zhang, Hongjian Yu, Yonghong Li, Fangli Liu, Wuxi Xie, and Ning Yan, *Propellants, Explos. Pyrotech.* 28 (3) (2003) 120–131.
- [4]. L.T. DeLuca, E. Marchesi, Spreafico, M.G. Colombo, A. Reina, S. Dossi, D. Consonni, and M. Brambilla, Agglomeration effects in metallized solid rocket propellants, theory and practice of energetic materials, vol. VIII, in *Proc. of IASPEP*, Li, S.-C., Wang, Y.-J., Cao, F.-X., Zhao, S.-S., and Zhou, S.-Q., eds., Science Press, pp. 258–270, 2009.
- [5]. W.Q. Pang, X.Z. Fan, *Application Progress of Metal Fuels in Solid Propellants (in Chinese)*, *Chem. Propellants Polym. Mater.* 7 (2009) 1–6.
- [6]. L.T. DeLuca, and L. Galfetti, Burning of metallized composite solid rocket propellants: From micrometric to nano-metric aluminum size, in *Proc. 3rd AJCPP*, Gyeongju, Korea, July, 2008.
- [7]. Pang Weiqiang, Luigi T. DeLuca, Xu Huixiang, Fan Xuezhong, Zhao Fengqi, Liu Fangli, Xie Wuxi, and Li Yonghong, *International Journal of Energetic Materials and Chemical Propulsion* 14 (4) (2015) 265–282.
- [8]. P.-X. Xu, *The Rheology of Polymer and its Applications*, Chemical Industry Press, Beijing, 2003.
- [9]. Wei-Qiang Pang, Xue-Zhong Fan, Feng-Qi Zhao, Wei Zhang, Hui-Xiang Xu, Hong-Jian Yu, Wuxi Xie, Ning Yan, and Fang-Li Liu, *Propellants, Explos. Pyrotech.* 39 (2014) 3290–336.
- [10]. V.A. Babuk, I. Dolotkazhin, A. Gamsov, L.T. DeLuca, and L. Galfetti, *J. Propul. Power* 25 (2) (2009) 482–489.
- [11]. K.K. Kuo, *Combustion of Boron Based Solid Propellant and Solid Fuels*, CRC Press, Boca Raton, 1993, pp. 375-384.
- [12]. L.T. DeLuca, L. Galfetti, G. Colombo, F. Maggi, and A. Bandera, *J. Propul. Power* 26 (4) (2010) 724–733.
- [13]. R.A. Yetter, G.A. Risha, and S.F. Son, *Proc. Combust. Inst.* 32 (2009) 1819–1838.
- [14]. A.E. Medvedev, A.V. Fedorov, V.M. Fomin, *Mathematical Modeling of Metal Particle Ignition in the High Temperature Flow Behind a Shock*, *Combust. Explos. Shock Waves (Engl. Transl.)* 1982, 18, 261–264.
- [15]. V.A. Babuk, V.A. Vasilyev, and V.V. Sviridov, Formation of condensed combustion products at the burning surface of solid rocket propellant, in Yang, V., Brill, T. B., and Ren, W.Z., eds., *Solid Propellant Chemistry, Combustion, and Motor Interior Ballistics*, Progress in Aeronautics and Astronautics, AIAA, Reston, VA, pp. 749–776, 2000.
- [16]. P.D. Lightfoot, Q.S. M. Kwok, A.-M. Turcotte, R.C. Fouchard, W. Ridley, and D.E.G. Jones, *Characterisation of Aluminium Nanopowders*,

- Combustion Institute Canadian Section Spring Technical Meeting, Montreal, QC, Canada, 13-16 May 2001.
- [17]. L. Merotto, L. Galfetti, G. Colombo, and L.T. DeLuca, Characterization of nAl powders for rocket propulsion, *Progress in Propulsion Physics*, EDP Sciences, 2 (2011) 99–120.
- [18]. R.A. Yetter, and G.L. Dryer, Metal particle combustion and classification, *Microgravity Combustion: Fire in Free Fall*, Academic Press, New York, pp. 419–478, 2001.
- [19]. Y.S. Kwon, A.A. Gromov, A.P. Ilyin, E.M. Popenko, and G.H. Rim. *Combust. Flame* 133 (2003) 385–391.
- [20]. I.M.K. Ismail and T.W. Hawkins, Evaluation of Electro Exploded Aluminum (ALEX) for Rocket Propulsion, CPIA Publication 1996, 650 (2), 25.
- [21]. L. Meda, G.L. Marra, R. Braglia, L. Abis, R. Gallo, F. Severini, L. Galfetti, and L.T. DeLuca, A wide characterization of aluminum powders for propellants, in *Proc. of the 9-IWCP, Novel Energetic Materials and Applications*, Grafiche G.S.S., Bergamo, November, Paper no. 17, 2004.
- [22]. C. Johnson, T. Parr, D. Hanson-Parr, R. Hollins, S. Fallis, and K. Higa, Combustion and oxidation of metal nanoparticles and composite particles, in *Proc. of 37th JANNAF Meeting*, Nov. 13-17, p. 539, 2000.
- [23]. D.E.G. Jones, P. Brousseau, R.C. Fouchard, A.-M. Turcotte, and Q.S.M. Kwok. *J. Therm. Anal. Calorim.* 61 (2000) 805–818.
- [24]. Development of Sensitivity Tests at the Explosive Research Laboratory (Ed.: D. H. Mallory), Bruceton Pennsylvania, NAVORD, Report No. 4236, 1960.
- [25]. J.K.G. Peters, Production Program of Julius Peter Company for Members of M. B. B., Course-81, Berlin, 1921, pp. 14–20.
- [26]. G.V. Ivanov and F. Tepper, Activated Aluminum as a Stored Energy Source for Propellants, in: K. K. Kuo (Eds), *Challenges in Propellants and Combustion 100 Years After Nobel*, Begell House, New York, 1997, p. 636.
- [27]. Luigi T. De Luca, Edward W. Price, Martin Summerfield. *Nonsteady Burning and Combustion Stability of Solid Propellants [M]*. Vol. 143, *Progress in Astronautics and Aeronautics*, American Institute of Aeronautics and Astronautics, 1992.
- [28]. N. Eisenreich, H. Fietzek, M. Del Mar Juez-Lorenzo, V. Kolarik, A. Koleczko, and V. Weiser. *Propellants, Explos. Pyrotech.* 29 (3) (2004) 137–145.
- [29]. Alexander Gromov, Ulrihc Teipel. *Metal Nanopowders - Production, Characterization and Energetic Applications[M]*. WILEY-VCH, 2014.
- [30]. X.-G. Wu, Q.-L. Yan, X. Guo, X.-F. Qi, X.-J. Li, and K.-Q. Wang, *Acta Astronaut.* 68 (7-8) (2011) 1098–1112.