

Full Paper

Research on the Combustion Properties of Propellants with Low Content of Nano Metal Powders

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Abstract

A comparison of various experimental results for combustion-related properties evaluation, including burning rates, deflagration heat, flame structures and thermal decomposition properties, of AP/RDX/Al/HTPB composite propellants containing nano metal powders is presented. The thermal behavior of n-Al (nano grain size aluminum) and g-Al (general grain size aluminum i.e., 10 μm) heated in air was also investigated by thermogravimetry. The burning rates results indicate that the usage of bimodal aluminum distribution with the ratio around 4:1 of n-Al to g-Al or the addition of 2% nano nickel powders (n-Ni) will improve the burning behavior of the propellant, while the usage of grading aluminum powders with the ratio 1:1 of n-Al to g-Al will impair the combustion of the propellant. Results show that n-Al and n-Ni both have a lower heating capacity, lower ignition threshold and shorter combustion time than g-Al. In addition n-Al is inclined to burn in single particle form. And the thermal analysis results show that n-Ni can catalyze the thermal decomposition of AP in the propellant. The results also confirm the high reactivity of n-Al, which will lead to a lower reaction temperature and rather higher degree of reaction ratio as compared with g-Al in air. All these factors will influence the combustion of propellants.

Keywords: Nano Aluminum Powders, Nano Nickel Powders, Composite Propellant, Combustion Properties

1 Introduction

"Nano" represents 10^{-9} , an extremely small quantity with enormous implications for the miniaturization-driven technology of the twenty-first century. Nanostructure materials, defined to describe materials characterized by structural features of less than 100 nm in average size, have exhibited high chemical reactivity associated with the ultra-fine grain size of nano particles, which allows a number of metals to undergo reactions that were previously considered impossible. Therefore there is a growing interest in nano metal powders in general. In the area of aerospace, scientists and

engineers typically have been interested in the synthesis and fabrication of new types of propellants containing nano metal powders [1–20]. The culmination of that research is the successful preparation of an ultra-fine aluminum powder, Alex, through plasma explosion process for combustion applications [1].

Alex has exhibited a quite different combustion performance compared with conventionally used aluminum powders. Adding Alex to hybrid engine fuels was proposed by a Penn State University team, who found that adding 20% Alex to HTPB fuel increased recession rate by 40% and mass burning rate by 70% [2]. Corresponding experimental results have revealed the unique thermal behavior of n-Al, which can contribute effectively to the burning behavior of the propellant and improve the propellant's combustion characteristics [3, 4]. Therefore, the Alex propellant seems to be useful as an additional accelerator for projectiles, and also as an igniter or as a booster for applications in high-pressure rocket propulsion.

While most investigations have shown beneficial effects of the addition of ultrafine aluminum to AP composite propellant [1–20], a few studies have shown that the incorrect application of nano metal powders will also lead to some negative consequences in other formulations. For example, our research has pointed out that, in certain formulations, the addition of nano metal powders with high content will lead to a honeycombed surface on the propellant, due to the complex interactions among the solid propellant ingredients and nano metal powders. And the combustion characteristics of propellants containing nano aluminum powders may also be not ideal in some formulations or in certain pressure ranges, as shown in this paper for the AP/RDX/Al/HTPB composite propellant. At the same time, because ultra-fine aluminum will provide less particulate damping in rocket motors, the propellant containing Alex will exhibit unstable combustion behavior [11, 13]. This very important point should be taken into account

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when treating and generalizing the data for propellants with pure Alex [11]. In addition, although extensive research has been done by various authors in understanding the fundamental combustion mechanisms and combustion instability in AP composite propellants, the exact mechanism responsible for the beneficial characteristics of AP/RDX/Al/HTPB with nano Ni based propellants is still obscure. Thus, it would be desirable that similar research will be carried out more widely and deeply, especially on the effects of nano grain size aluminum (n-Al) or some other nano metal powders. So in the same basic formulation, besides the first glance at the effects of n-Al (90 nm), the effects of nano nickel powders (n-Ni, 60 nm) are also taken into consideration. An interpretative mechanism for the effects of nano metal is developed. These studies may offer some clues for the appropriate application of nano metal powders in propellant and help to obtain better control of their ignition, combustion, and/or sensitivity. These issues are the main topic of this paper.

2 Experimental Results

2.1 Experimental Formulations

The basic formulations of the samples consisted of HTPB, AP (80 μm), aluminum, and RDX (320 μm), in which the amount of general grain size aluminum (g-Al, 10 μm) is 5%. The n-Al and n-Ni were applied to compose three different formulations. The detailed formulations used in this study are shown in Table 1.

2.2 Burning Rates

All burning rates measurements were performed with a strand burner which was pressurized with nitrogen. The burning rates were measured at five different pressures

Table 1. Formulations of the Samples.

Propellants' Sample Num.	HTPB (%)	AP (%)	RDX (%)	g-Al (%)	n-Al (%)	n-Ni* (%)
N-0	15	60	20	5	0	–
N-1	15	60	20	2.5	2.5	–
N-2	15	60	20	1	4	–
N-3	15	60	20	5	0	2

* external addition

Table 2. Content of Nano Metal Powders and Burning Behavior of the Samples.

Propellant Sample	Burning rate (mm/s) under different Pressure (MPa)					Pressure Exponential n
	2	4	6	8	10	
N-0	5.73	7.96	9.96	11.30	12.48	0.485
N-1	5.63	7.57	8.96	9.97	10.81	0.401
N-2	6.24	8.21	9.51	10.90	11.78	0.398
N-3	6.04	8.21	9.51	10.38	10.98	0.360

(2 MPa, 4 MPa, 6 MPa, 8 MPa and 10 MPa) in a constant temperature of 20 °C. The burning rate results were fitted to the Vieille burning rate equation

$$r = aP^n \quad (1)$$

where r , a , P , and n are the burning rate, an experimental constant, chamber pressure, and the pressure exponent, respectively. The experimental results are listed in Table 2 and Fig. 1.

As compared with the basic formulation N-0, the burning rate of N-1 decreased in the experimental pressure ranges. And the burning rate of N-2 and N-3 increased in the low-pressure ranges. The amount of enhancement will decrease with the increase of pressure. And the pressure exponent of N-2 and N-3 is 0.087 and 0.125 lower than N-0 respectively.

2.3 Deflagration Heat

The propellant's deflagration heat was measured by the thermostatic oxygen bomb calorimeter, in N₂ atmosphere. The average value of three experimental measurements for every sample is listed in Table 3.

As compared with the basic formulation N-0, the deflagration heat of N-3 decreased 77 kJ/kg, due to the relatively lower heating capacity of n-Ni (4.1 MJ/kg) compared with that of conventionally used Al (31 MJ/kg) [7].

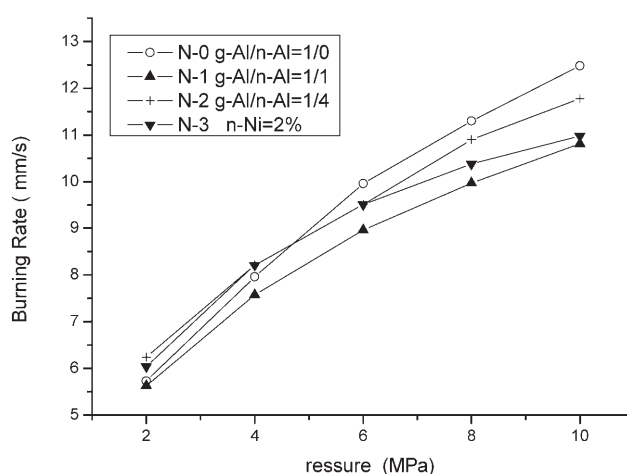


Figure 1. The burning rate of propellant as a function of pressure.

Table 3. Deflagration-heat measuring results.

Propellant Sample	N-0	N-1	N-2	N-3
Annotation	g-Al : n-Al = 1 : 0	g-Al : n-Al = 1 : 1	g-Al : n-Al = 1 : 4	2% n-Ni
Deflagration Heat (kJ/kg)	5315	5261	5314	5238

As compared with the basic formulation N-0, the deflagration heat of N-1 decreased 54 KJ/kg. In the simplest view, one might then assume that replacing more parts of g-Al with n-Al in N-2 would result in less deflagration heat as compared with N-1. This simple view however is not supported by the results. Table 3 shows that the deflagration heat of N-2 with g-Al : n-Al = 1 : 4 is greater than that of N-1 with g-Al : n-Al = 1 : 1, and is almost identical with that of the N-0.

In the several propellant formulations studied in this paper (N-0, N-1, N-2), the aluminum coarse-to-fine ratio is the only varied factor, so the differences appearing in deflagration heat result mainly from this factor. We suggest that the addition of n-Al will have an influence on the energetic properties of the propellant as illustrated below.

On the one hand, when the oxidizer decomposes, heat will be released and transferred to aluminum powders. Due to its small average size and large specific surface area, the diffusion distances between the oxidizer and the n-Al fuel will be decreased significantly and the availability of the oxidizer species for the n-Al will be increased subsequently. Hence the aluminum particle can be easily heated to a higher temperature, and the “local heat point” can be formed. In consequence, the “local heat point” strengthens the interaction and releases extra heat, which can further increase the propellant’s thermal decomposition reaction heat.

On the other hand, previous study [15] has revealed that compared with conventionally used aluminum particles (20 μm – 40 μm) whose active aluminum content was 99%, the content of active metal in ultra-fine Al powders (< 30 nm) was only between 80% and 86%. Due to n-Al’s rather higher volumetric percentage of inert oxide coating and higher content of absorbed inert gas on the particle surface, the total energy of oxidation released per unit volume of g-Al particles will be greater than that of n-Al particles. When we consider this factor only, in consequence, the addition of n-Al in the propellant will lead to less heat released, which can further decrease the propellant’s thermal decomposition reaction heat.

Based upon the above-mentioned point, N-1 with g-Al : n-Al = 1 : 4 will be classified as the dominating effect of the latter factor, which predicts less decomposition reaction heat. Meanwhile N-2 with g-Al : n-Al = 1 : 1 counterbalances the two factors. With the increase in the content of n-Al, the probability for the oxygen-rich products produced during the decomposition of oxidants to diffuse to n-Al surface is relatively large. It is much easier to form a “local heat point” with the aluminum particle as the center, which will lead to significant increase of the heat released during the thermal decomposition of the propellant, although the

total energy of oxidation released per unit volume of mixed Al particles will decrease simultaneously with the increase of the content of Al. It seems that, in N-2 with g-Al : n-Al = 1 : 1, the extra heat released due to the former factor will offset that of the latter factor, resulting in unchanged decomposition reaction heat.

2.4 Observation of Flame Images

The flame characteristics of the burning samples were observed in the combustion chamber. At the low pressure (2 MPa), the combustion of sample without nano metal powders (N-0) and N-1 with g-Al : n-Al = 1 : 1 shows a large fraction of the Al burning as very large agglomerates away from the surface, while sample N-2 (with g-Al : n-Al = 1 : 4) and N-3 (with n-Ni) have rather smaller agglomerates with fairly even bright flame. The region above the surface was luminous, starting very close to the surface. At the high pressure, the combustion of all the samples becomes more violent. This tendency is more noticeable in samples N-2 and N-3. Intense bright flames were found to be formed successively near the sample surface of N-2 and N-3.

Parr applied planar laser-induced fluorescence (PLF), and UV/visible absorption spectroscopy to a class of nano aluminum based propellants to study the AIO in the flames [8]. The AIO concentration on the surface of conventionally used 5 μm propellant was found to be 50 – 70 ppm. However, AIO concentration from one of the nano-aluminum propellants was as high as 130 ppm, showing faster combustion of the nano-aluminum compared to that of 5 μm Al. Their experiments showed that a strong flame with relatively high AIO concentration is close to the surface, which suggest that some of the nano-aluminum was burning relatively close to the surface [6, 8]. The flame structure observed in our experiments is in agreement with the results of Dokhan et al. [6] and Parr et al. [8].

2.5 TG – DTA Results of Propellant in Nitrogen

In order to investigate the effects of nano metal powders on thermal decomposition properties of the propellant, differential thermal analysis (DTA) – thermogravimetry (TG) on-line operation techniques were adopted to measure the three propellant samples. The tests of thermal decomposition were performed with a Mettler TA2100 DTA – TG analysis in a dynamic atmosphere of nitrogen at a scanning rate of 10 °C per minute. The TG – derivative thermogravimetry (DTG) curves of N-0 show three obvi-

ously distinguished mass loss stages (Fig. 2). The first stage is accompanied by about 19% mass loss in temperature ranges of 200 °C–244 °C corresponding to the thermal decomposition of RDX. The second stage is accompanied by about 23% mass loss in temperature ranges of 244 °C–322 °C (i.e., the stage of low temperature decomposition AP). The third stage is accompanied by about 38% mass loss in temperature ranges of 322 °C–387 °C (i.e., the stage of high temperature decomposition AP). Our previous study has pointed out that nano nickel powders are active in promoting the thermal decomposition of AP while aluminum powders are nearly inactive [9]. We find thermal decomposition tests of our formulations are in agreement with such conclusions. The thermal decomposition traces of formulation N-2 were only slightly different from those of N-0. The TG–DTG–DTA curves of N-3 are shown in Fig. 3. Fig. 3 indicates that due to the addition of n-Ni, the temperature of the first and second exothermal peak of the AP is lowered by 6 °C and 8 °C, respectively. And n-Ni will also reduce the DTG peak of the AP about 7.0 °C. Such catalysis effects of n-Ni will be one of the important factors that influences the combustion behavior of propellant, as we will discuss below.

The results also indicate that the thermal decomposition peak relating to RDX in Fig. 3 is similar to that in Fig. 2, suggesting the minor influence of n-Ni on the thermal decomposition of RDX in the formulations.

2.6 TG–DTG Results of Aluminum in Air

In order to investigate the thermal behavior of aluminum particles in air, a Mettler TA2950 thermogravimetry (TG) analysis was employed at a scanning rate of 20 °C per minute in dynamic air atmosphere. An almost constant sample mass of 2.0 ± 0.1 mg was used in all experiments. The flow rate of air in all TGA experiments was 100 mL/min. The TG–DTG experiments on the two kinds of powdered aluminum with the different particle size (10 μ m, 90 nm) were carried out, and the results are shown in Figs. 4 and 5, respectively. It is shown that aluminum particles in air have undergone a multi-stage process with the increase of temperature. The thickness of the oxide region increases linearly with time and is not saturated at the initial stage of oxidation. The onset of the initial oxidation reactions of n-Al occurs at a

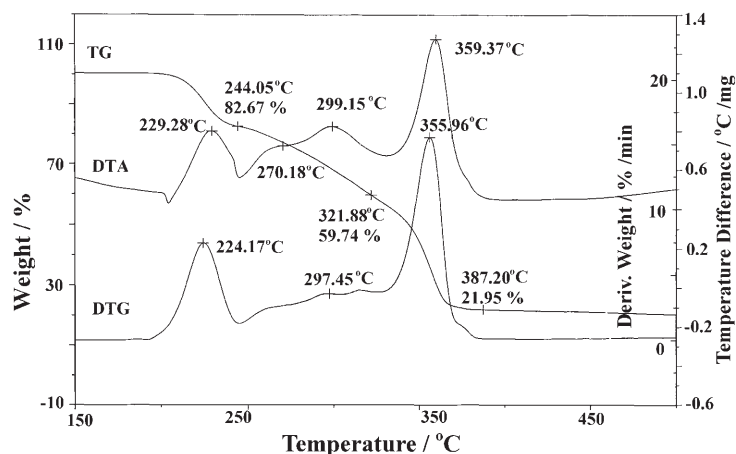


Figure 2. Thermal Analysis Curves of N-0 (0.1 MPa; 10 °C/min).

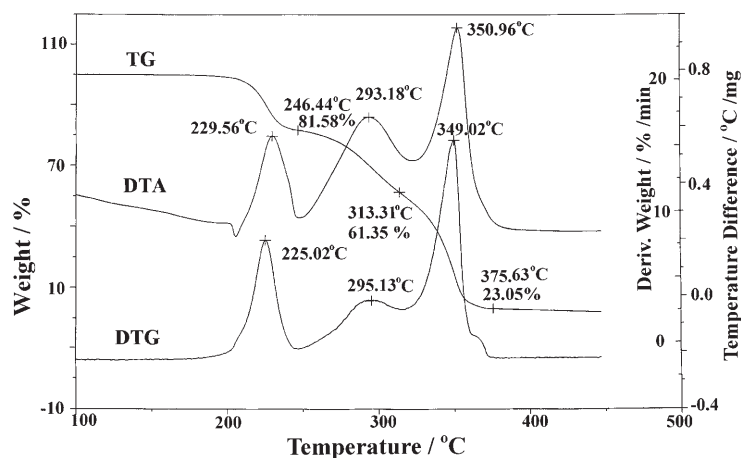


Figure 3. Thermal Analysis Curves of N-3 (0.1 MPa; 10 °C/min).

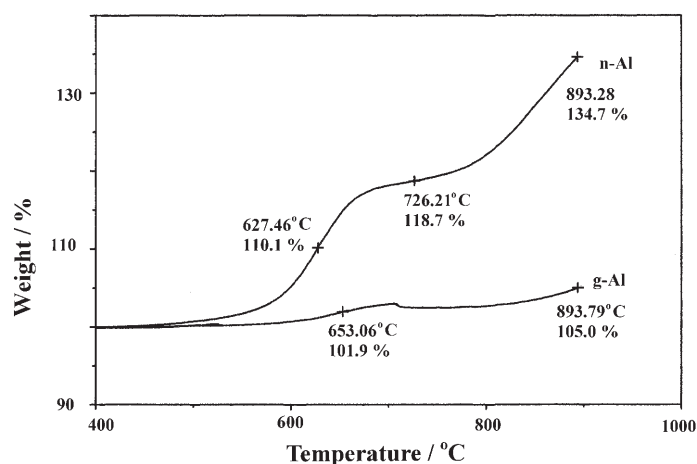


Figure 4. TG Curves of n-Al and g-Al (0.1 MPa; 20 °C/min).

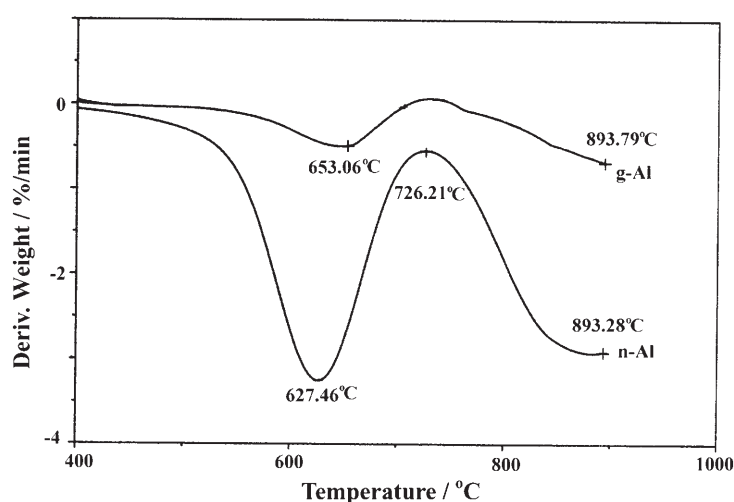


Figure 5. DTG Curves of n-Al and g-Al (0.1 MPa; 20 °C/min).

threshold temperature of around 400 °C. At around 628 °C, the initial oxidation reactions show one sharp DTG peak with a conversion ratio at 10.1%. The second stage reaction of n-Al, which results in a weight gain, has a threshold temperature of around 726 °C. This is believed to be associated with the aluminum nitride formation process [15]. Due to the temperature limit of the instrument, the experiment is broken off at around 893 °C with the conversion ratio of n-Al at 35%.

The TG trace of g-Al in air is different from that of n-Al powders. It has one small weight DTG peak at around 653 °C with a conversion ratio of only 2%. And the conversion ratio at 894 °C is 5%, which is about 30% lower than that of n-Al. This difference could be due to the high reactivity of n-Al, leading to a lower reaction temperature and a rather higher degree of reaction ratio.

An oxidation study of metal powders in air provides an opportunity to measure the effects of particle size on some important physio-chemical properties of metal powders, such as the ignition threshold energy. It is known that n-Al

has an extremely rapid weight gain at around 628 °C with a high degree of reaction ratio, which corresponds to vigorous heat release around its melting point (660 °C for pure aluminum). The experiments on the combustion of aluminum particles in air have revealed that although most of the metal is oxidized in the vapor phase, heterogeneous metal/oxygen interaction processes affect the combustion scenario significantly [16, 17]. Since the surface oxidation-reduction reaction heat is approximately proportional to the surface area, when the aluminum particle size is smaller than a certain critical value the aluminum particles (n-Al) will be rapidly heated before an appreciable deposit of Al_2O_3 on their surfaces can occur, leading to a progressive self-acceleration of heating due to the reactions between Al and the oxidizer. Such heat from self-acceleration released during the surface oxidation reaction will be enough to cause ignition at much lower temperatures than the melting point, and the n-Al will then tend to ignite as single particles in the combustion process of propellant. However, in the present experiment, the g-Al powders are two orders of

magnitude larger than the n-Al powders and also have shown rather inert reactivity. And as we have seen above, such definitely different oxidative behavior will be one important factor in different combustion behaviors.

Ivanov et al. have previously suggested that the source of the unique combustion behavior of the ultra-fine aluminum powders Alex, i.e., the burning enhancement behavior unlike that of ordinary aluminum powders, might be the stored internal energy of Alex, which can be released in an exothermic reaction at a relatively low threshold temperature [1]. But Fig. 5 shows that the shape of the DTG traces of n-Al is similar to that of g-Al. And n-Al will reach its oxidation peak just before its melting point with a threshold temperature of around 400 °C, while Alex will release the stored internal energy at a threshold temperature of 450 °C [1]. Such results in turn suggest that the characteristics of the reactions in air for n-Al and g-Al all follow the same trends, although the n-Al has exhibited rather higher reactivity. As for the overlap of the oxidation exothermic process and the proposed stored energy released process, the stored energy of n-Al may be negligible due to the dominant influence of the former phenomenon. Based on the theoretical model of the process of energy storage developed by means of the compression of the liquid portion of an Alex particle by its shrinking solid shell during rapid solidification of the particle, DeSena, also has concluded that, although the postulated mechanism could store energy, the amount of stored energy was realistically negligible [18]. This theoretical finding is in agreement with our experiments and other research [4] that no evidently stored energy release phenomenon is observed in n-Al particles.

3 Discussion

3.1 The Influence of n-Al on the Combustion Behavior of the Propellant

The experimental results above indicate that in AP/RDX/HTPB composite propellants, the usage of bimodal aluminum distribution with n-Al:g-Al = 4:1 in N-2 can effectively raise the propellant's burning rate and improve its combustion performance in low pressure range. Such enhancement will decrease with the increase of pressure, while the burning rate of N-1 with n-Al:g-Al = 1:1 all decreases compared with N-0 in the pressure range tested. The influence of n-Al on the combustion properties is therefore described through which n-Al will influence the combustion characteristics of propellants.

There are many advantages of incorporating n-Al into propellants because of its rather ultra-fine grain size, such as: 1) shortened ignition delay; 2) shortened burning times, resulting in more complete combustion in propulsion systems; 3) nano-sized aluminum can be dispersed into a high-temperature zone for direct oxidation reaction and rapid energy release; 4) enhanced heat absorptivity of propellant for the band absorptivity of nano metal powders due to its rather ultra-fine grain size [21].

There are also some shortcomings of incorporating n-Al into propellants, such as: 1) the lower content of active Al in n-Al will lead to less energy released per unit volume of n-Al particles than that of g-Al particles; 2) the complex interactions among the solid propellant ingredients and nano metal powders during the moulding process will lead to difficulty in designing new formulations.

In these specific AP/RDX/HTPB/Al composite propellants, these factors will work together to influence the combustion behavior of the propellants as discussed in the experimental section.

It should be noted that there are two different kinds of oxidants, AP and RDX, in this composite propellant. The flame structure of the AP/RDX propellants consists of two types of flames: one type is the diffusion flame produced by the decomposed gases of the AP particles and the binder; the other type is the premixed flame produced by the decomposed gases of the RDX particles and the binder [22]. According to the calculation results of the "two-zone" steady combustion model of AP/RDX composite propellant [23], when the content of AP > 50%, the AP will be the main oxidant. The burn rate and the combustion index are mainly controlled by the diffusion flame produced by the decomposition products of AP and the binder [23, 24].

The melting of RDX and formation of a melt layer of RDX-HTPB binder will act as a thick barrier between AP particles. This causes a decrease in the diffusion rate of fuel to the diffusion flame. We also know that in the condensed-phase reaction layer of nitramine particles such as RDX and HMX, two competitive processes exist: evaporation and exothermic decomposition [25]. The former one is the controlling step at low pressures, while the latter dominates at high pressures.

Then, in low pressure range, for this specific AP/RDX/HTPB/Al composite propellant with the AP = 60%, the ability to ignite the Al close to the propellant surface is thought to be achieved by the near-surface hot AP/binder flamelets called "LEF – Leading Edge Flames", as they are the only sources that are hot enough to achieve this [12, 26, 27].

The flame characteristics of the burning samples observed show that at the low pressure (2 MPa), the combustion of the sample without nano metal powders (N-0) shows a large fraction of the Al burning as very large agglomerates away from the surface, while sample N-2 (with g-Al:n-Al = 1:4) has rather smaller agglomerates with fairly even bright flame. As we have seen above, the region above the surface was luminous, starting very close to the surface. The proximity of the luminous region to the propellant's surface would allow for greater heat feedback to the flame front for higher burn rates. While the intensity and location of the bright near-surface flames were not quantified, these properties were qualitatively consistent with the argument that such flames contribute to burning rates (and the extraordinary brightness establishes that near-surface Al combustion is involved).

Returning to the mechanistic arguments, the bright near-surface flames seen where n-Al is used are indication of

enhanced Al burning. We know that, while at low pressures the leading edge flame moves far away from the combustion surface [27], it is unfavorable for the ignition of accumulating aluminum and large agglomerates. They will gather, melt, connect and agglomerate with each other on the surface, finally ignite to enter the gas phase. Then the sample of N-0 without addition of n-Al shows a large fraction of the Al burning as very large agglomerates away from the surface.

N-Al experiences different physical and chemical processes from g-Al on the combustion surface propellants, where the surface-melting layer forms when the propellant burns. Since the n-Al will significantly release heat near 600 °C (illustrated in Fig. 4 and Fig. 5) and the temperature of the surface-melting layer is between 600 and 900 K [28], the effect of n-Al to raise the burning rate of the propellants is therefore attributed to n-Al's combustion and its released heat.

By virtue of n-Al's rather active oxidation properties (as shown in Fig. 4 and Fig. 5) and its fairly low ignition energy threshold, when the burning surface withdraws to expose n-Al, the forced early ignition of n-Al in the flame zone is expected to occur before particles have time to accumulate or agglomerate on the burning surface. The majority of those aluminum particles can directly enter the gas phase to burn in single particle mode and their agglomeration can be effectively prevented. Then n-Al will mainly ignite on or near the combustion surface [14]. Due to the relatively high particle emissivity of burning Al particles in the aluminized propellant, $\varepsilon = 0.9$ [29], such near combustion surface burning behavior will lead to a rather greater amount of heat-flux feedback from the burning of n-Al to the unburnt surface than that of g-Al particles.

At the same time, one should also recognize the negative effect of n-Al on the burning rate of propellants for the lower content of active Al in n-Al, which will lead to less energy released per unit volume of n-Al particles than that of g-Al particles on the combustion surface of propellants.

In general, the burning rate of solid propellants is closely proportional to heat feedback from the gas phase to the burning surface [22]. It seems that for N-2 at higher n-Al concentrations, the promoting effects of n-Al were the dominant factor, which would lead to a greater amount of heat-flux feedback from the burning of n-Al to the unburnt surface, resulting in an increased burning rate. However for N-1 with n-Al:g-Al = 1:1, the heat-flux feedback from the burning of small quantities of n-Al to the unburnt surface cannot effectively contribute to the combustion and the negative effects were the dominant factor, which in turn decreases the burning rate. Such inference is correlated with the burning rate results and observed properties of flame structures in low pressure range.

With an increase in pressure, the leading edge flame moves closer to the propellant surface. We also know that the gas exothermic decomposition of RDX dominates at high pressures [25], since the gas decomposition products of RDX such as N_2O , NO, NO_2 etc., have a high concentration in the gas composition [30]. And previous studies have

suggested that nitrogen oxides are excellent oxidizers for Al at high temperature [31]. Consequently aluminum in nitramine propellant may also be oxidized by gas decomposition products of RDX in high pressure range. All these, including the closer leading edge flame, the highly exothermic gas decomposition of RDX and the oxidation reaction between Al and nitrogen oxides at the burning surface will provide Al ignition. The g-Al's percentage of burning in single particle mode and combustion efficiency will increase simultaneously. The thickness of the surface-melt layer will also decrease with the increase of pressure, which will make less n-Al burn in single particle mode on the surface-melt layer and more g-Al particles easily pushed into the gas-phase flame position by an impetus from combustion gases [32]. At the same time, the heat of interaction between the reaction layer of the condensed phase and hot portions of the gas phase will be very slight because the distances between the burning surface and the hot flame position are much larger than the conductive length scale [33]. The burning rates of the propellant will then be raised at high pressures not because of the grain size of aluminum, but because of the presence of aluminum itself. Due to the g-Al's relatively high energetic properties, the heat feedback and burn rates will therefore decrease especially for n-Al in N-1 and N-2 as compared with that of N-0. This tendency is also in agreement with the data represented in Table 1.

3.2 The Influence Mechanism of n-Ni on the combustion Properties of the Propellant

The experimental results above indicate that in AP/RDX/HTPB composite propellants, the addition of 2% nano nickel powders (n-Ni) can also effectively raise the propellant's burning rate and improve its combustion characteristics. The amount of enhancement will decrease with the increase of pressure. And the propellant's pressure exponent is reduced below that with the use of g-Al alone. We then suggest a dual role of n-Ni in promoting combustion behavior.

In the combustion process of propellant, n-Ni will act as a fuel and have a similar role to aluminum powders. At low pressures, the thickness of the surface-melt layer and the condensed-phase reaction fraction are relatively large. Since the regression rate of the AP particles is less than that of the binder, AP crystals will protrude above the binder [34]. Large amounts of oxygen-rich products produced during the decomposition of AP, such as $HClO_4$ (g), may diffuse through the binder surface-melt layer and migrate to the n-Ni surface by surface diffusion. Then n-Ni will mainly ignite on the propellant surface and the increased heat feedback will efficiently raise the propellant's burning rate.

On the other hand, n-Ni will also act as a burning rate catalyst. In the combustion process, the most dominant catalysis effect of n-Ni is promoting the pyrolysis of AP at or near the surface-melting layer. AP's condensed-phase decomposition will then be promoted subsequently. Such

promoting effects will then cause the release of more active gases abundant in oxygen or chlorine, which will then participate in the chain reaction, enhance gas-phase reactions, increase the heat feedback to the combustion surface and raise the burning rate.

At the same time, such catalysis effect will also promote the combustion of aluminum. Based on the detection of oxygen in the interiors of the particles partially burned in different gas mixtures, Dreizin et al. have confirmed that the oxygen dissolution is a generic process occurring in aluminum combustion in oxygenated environments [16, 17]. Due to the catalysis effect of n-Ni, large amounts of oxidative gases will be produced. In the locations where the oxygen-rich phase is produced, the rate of inward oxidative gases transporting to the aluminum powders becomes greater. The probability of oxide cap formation will be greater when the process of oxygen dissolution occurs more actively, which clearly is very beneficial for rapid and complete aluminum combustion [16, 17]. Such a beneficial mechanism provides a basis for interpreting the observed decrease of Al burning as very large agglomerates away from the surface in the flame structure. Therefore the rise of the propellant's (N-3) burning rate and improvement of its combustion characteristics can be ascribed to the two mutual beneficial effects of n-Ni mentioned above.

As the pressure is increased, the high regression rate of the burning surface will decrease the thickness of the surface-melting layer and the condensed-phase reaction fraction. Since n-Ni will act as a burning rate catalyst to promote the pyrolysis of condensed-phase AP at or near the surface-melting layer, the decrease of the condensed-phase reaction fraction will make less time or probability for Ni to take effect. And the promoting effect of n-Ni on the thermal decomposition of AP (condensed-phase) will then be weakened subsequently. However, the relatively lower heating capacity of n-Ni will be the dominant factor to inhibit combustion.

4 Conclusions

In composite propellants, the addition of 2% nano nickel powders (n-Ni) or the usage of bimodal aluminum distribution with the ratio around 4:1 of nano aluminum (n-Al) to general aluminum (g-Al) can effectively raise the propellant's burning rate and improve its combustion characteristics, while the propellant's pressure exponent is reduced below that with the use of g-Al alone. Besides the adjustment of the basic formulation, further improvement can be accomplished by combination usage of nano metal powders or surface treatment of powdered nano aluminum powders etc., based on more appropriate physical chemistry methods established in the future and better comprehension of the complex interactions among the nano metal powders and all other solid propellant ingredients.

5 References

- [1] G. V. Ivanov, F. Tepper, Activated Aluminum as a Stored Energy Source for Propellants, in K. K. Kuo, et al., (Eds.), *Challenges In Propellants And Combustion 100 Years After Nobel*, Begell House, New York, **1997**, p. 636.
- [2] M. J. Chiaverini, K. K. Kuo, A. Peretz, G. C. Harting, Heat Flux and Internal Ballistic Characterization of a Hybrid Rocket Motor Analog, *33rd AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit*, Seattle, WA, July 6–9, **1997**, AIAA 1997–3080.
- [3] M. M. Mench, C. L. Yeh, K. K. Kuo, Propellant Burning Rate Enhancement and Thermal Behavior of Ultra-Fine Aluminum Powders (Alex), *29th Int. Annual Conference of ICT*, Karlsruhe, Germany, June 30–July 3, **1998**, p. 30/1.
- [4] M. M. Mench, K. K. Kuo, C. L. Yeh, Y. C. Lu, Comparison of Thermal Behavior of Regular and Ultra-fine Aluminum Powders (Alex) Made From Plasma Explosion Process, *Combust. Sci. Technol.*, **1998**, *135*, 269.
- [5] N. Kubota, Y. Yano, T. Kuwahara, Particulate Damping of Acoustic Instability in RDX/AP Composite Propellant Combustion, *18th AIAA/SAE/ASME Joint Propulsion Conference*, Cleveland, Ohio, June 21–23, **1982**, p. 82–1223.
- [6] A. Dokhan, E. W. Price, J. M. Seitzman, R. K. Sigman, The Effects of Bimodal Aluminum with Ultrafine Aluminum on the Burning Rates of Solid Propellants, *29th International Symposium on Combustion*, Sapporo, Japan, **2002**, p. 2939.
- [7] D. A. Yagodnikov, A. V. Voronetskii, Experimental and Theoretical Study of the Ignition and Combustion of Aerosol of Encapsulated Aluminum Particles, *Combust. Explo. Shock*, **1997**, *33*, 49.
- [8] T. P. Parr, D. M. Hanson-Parr, Flame Structure Studies of Ultrafine-aluminum Containing Propellants, *JANNAF 35th Combustion Subcommittee Meeting*, Tucson, Arizona, December 7–11, **1998**, p. 593.
- [9] Z. Jiang, S. F. Li, F. Q. Zhao, et al., Thermal behavior of AP and Metal Powders of Different Grade, *J. Therm. Anal. Calorim.* **2006**, *83*, DOI 10.1007/s10973-005-7035-7.
- [10] A. Pivkina, P. Ulyanova, Y. Frolov, S. Zavayalov, J. Schoonman, Nanomaterials for Heterogeneous Combustion, *Propellants, Explos., Pyrotech.* **2004**, *29*, 39.
- [11] V. N. Simonenko, V. E. Zarko, Comparative Studying of the Combustion Behavior of Composite Propellants Containing Ultrafine Aluminum, *30th Int. Annual Conference of ICT*, Karlsruhe, Germany, 29 June–2 July, **1999**, p. 21/1.
- [12] A. Dokhan, E. W. Price, J. M. Seitzman, R. K. Sigman, Combustion Mechanisms of Bimodal and Ultra-Fine Aluminum in Ammonium Perchlorate Solid Propellants, *38th AIAA/ASME/ASE/ASEE Joint Propulsion Conference and Exhibit*, Indianapolis, Indiana, July 7–10, **2002**, AIAA 2002–4173.
- [13] F. Blomshield, S. Nguyen, H. Matheke, A. Atwood, T. Bui, Acoustic Particle Damping of Propellants Containing Ultra-Fine Aluminum, *40th AIAA/ASME/ASE/ASEE Joint Propulsion Conference and Exhibit*, Fort Lauderdale, Florida, July 11–14, **2004**, AIAA 2004–3722.
- [14] A. Dokhan, E. W. Price, J. M. Seitzman, R. K. Sigman, The Ignition of Ultra-Fine Aluminum In Ammonium Perchlorate Solid Propellant Flames, *39th AIAA/ASME/ASE/ASEE Joint Propulsion Conference and Exhibit*, Huntsville, Alabama, July 20–23, **2003**, AIAA 2003–4810.
- [15] V. G. Shevchenko, V. I. Kononenko, I. N. Latosh, et al., Effect of the Size Factor and Alloying on Oxidation of Aluminum Powders, *Combust. Explo. Shock*, **1994**, *30*, 635.
- [16] E. L. Dreizin, M. A. Trunov, Surface Phenomena in Aluminum Combustion, *Combust. Flame* **1995**, *101*, 378.
- [17] E. L. Dreizin, Experimental Study of Stages in Aluminum Particle Combustion in Air, *Combust. Flame* **1996**, *105*, 541.

- [18] J. T. DeSena, K. K. Kuo, Evaluation of Stored Energy in Ultra-fine Aluminum Powders Produced by Plasma Explosion, *J. Propul. Power*, **1999**, 15, 794.
- [19] A. Dokhan, *The Effects of Aluminum Particle Sizes on Aluminized Propellant Combustion*, PhD Thesis, School of Aerospace Engineering, Georgia Institute of Technology, Atlanta, GA, USA, July **2002**.
- [20] L. Meda, G. Marra, L. Galfetti, S. Inchingalo, F. Severini, L. De Luca, Nano-Composites for Rocket Solid Propellants, *Compos. Sci. Technol.* **2005**, 65, 769.
- [21] A. Ishihara, M. Q. Brewster, T. A. Sheridan, H. Krier, The Influence of Radiative Heat Feedback on Burning Rate in Aluminized Propellants, *Combust. Flame* **1991**, 84, 141.
- [22] T. Kuwahara, N. Kubota, Combustion of RDX/AP Composite Propellants at Low Pressures, *J. Spacecraft Rockets* **1984**, 21, 502.
- [23] W. Zhang, H. Zhu, W. Y. Liu, Calculation Study on Burning Rate Characteristic of AP/RDX/HTPB Propellants, *J. Propul. Technol.* **1997**, 18, 75 (in Chinese).
- [24] R. Muthiah, T. L. Varghese, S. S. Rao, K. N. Ninan, V. N. Krishnamurthy, Realization of an Eco-Friendly Solid Propellant Based on HTPB-HMX-AP System for Launch Vehicle Applications, *Propellants, Explos., Pyrotech.* **1998**, 23, 90.
- [25] C. Fang, S. F. Li, Synergistic Interaction between AP and HMX, *J. Energ. Mater.* **2002**, 20, 311.
- [26] E. W. Price, S. R. Chakravarthy, J. K. Sambamurthi, R. K. Sigman, R. R. Panyam, The Details of Combustion of Ammonium Perchlorate Propellants: Leading Edge Flame Detachment, *Combust. Sci. Technol.* **1998**, 138, 63.
- [27] E. W. Price, Combustion of Metalized Propellants, in K. K. Kuo, M. Summerfield (Eds), *Fundamentals of Solid Propellant Combustion*, American Institute of Aeronautics and Astronautics Inc. 1633 Broadway, New York, N.Y. 10019, Vol. 90 of Progress in Astronautics and Aeronautics, **1984**.
- [28] J. P. Renie, Temperature and Pressure Sensitivity of Aluminized Propellants, *16th AIAA/SAE/ASME Joint Propulsion Conference*, Hartford, Connecticut, June 30–July 2, **1980**, AIAA 1980–1166.
- [29] A. R. Ted, L. B. Rodney, Ignition and Combustion of Aluminum/Magnesium Alloy Particles in O₂ at High Pressures, *Combust. Flame* **1993**, 92, 125.
- [30] S. F. Palopoli, T. B. Brill, Thermal Decomposition of Energetic Materials 52. On the Foam Zone and Surface Chemistry of Rapidly Decomposing HMX, *Combust. Flame* **1991**, 87, 45.
- [31] J. Zhu, S. F. Li, Aluminum Oxidation in Nitramine Propellant, *Propellants, Explos., Pyrotech.* **1999**, 24, 224.
- [32] A. A. Zenin, Thermophysics of Stable Combustion Waves of Solid Propellants, in L. DeLuca, E. W. Price, M. Summerfield, (Eds), *Nonsteady Burning and Combustion Stability of Solid Propellants*, Progress in Astronautics and Aeronautics, AIAA, Washington D.C. Vol. 143, **1992**, p. 197.
- [33] L. H. Caveny, A. Gany, Aluminum Combustion Under Rocket Motor Conditions, AGARD-CP-259, **1979**, pp. 13–1.
- [34] T. L. Boggs, R. L. Derr, M. W. Beckstead, Surface Structure of Ammonium Perchlorate Composite Propellants, *AIAA Journal*, **1970**, 8, 370.

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