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Effects of Different Nano-Sized Metal Oxide Catalysts on the Properties of Composite Solid Propellants

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ABSTRACT

Several industrial- and research-type composite solid propellants containing different nano metric metal oxide catalysts (Fe_2O_3, Co_3O_4, CuO, and PbO) with similar nominal composition, were prepared and experimentally analyzed. The effects of different nano-sized metal oxide catalysts on the rheological properties and hazardous properties were investigated. The strand burning rate and the associated combustion flame structure of composite propellants were determined. The results show that the nano-sized metal oxide powders can be sufficiently dispersed in hydroxyl terminated polybutadiene binder. The propellant formulations containing nano metal oxide particles are sensitive to impact and friction except for the base propellant without nano-sized powders, which is less sensitive to friction as compared to the other compositions. The nano-sized metal oxide additives can affect the combustion behavior and increase the burning rate of propellants compared with the reference propellant composition.

KEYWORDS

Combustion property; Composite solid propellants; Hazardous property; Material chemistry; Nano-sized metal oxide particles

Introduction

Improving the performance of the solid propellants is always an important aspect for researchers, especially the combustion performance of propellants. Nano-sized particles, due to small particle size, large surface area, many surface atoms complex microstructures, and defects of grain, have high catalytic activity, therefore, replacing the conventional catalysts in solid propellant by nano-sized catalysts becomes a key researching hot point to improve the combustion performance of propellants (Babuk et al., 2009; DeLuca and Galfetti, 2008; Ishitha and Ramakrishna, 2014). The use of a new type of nano-sized catalyst with high catalytic activity is one of the important ways to improve the combustion properties of solid propellant. At present, a variety of publications were reported on the thermal decomposition of ammonium perchlorate (AP) by nano-scaled transition metal oxides, including manganese dioxide (MnO_2), nickel oxide (NiO), chromium trioxide (Cr_2O_3), iron oxide (Fe_2O_3), copper oxide (CuO), lead oxide (PbO), titanium dioxide (TiO_2), and their composite powders etc. (Babuk et al., 2000; Dey et al., 2015; Dubey et al., 2013; Verma and

Ramakrishna, 2013). It was found that 5% nano-sized Fe_2O_3 powder added to AP can decrease the first and the second thermal decomposition temperature of AP 61.89°C and 118.89°C, respectively (Chaturvedi and Dave, 2012; Gilbert et al., 2012). The heat of combustion of AP can be increased by 2.34 $kJ \cdot g^{-1}$ (pure AP is 16.70 $kJ \cdot g^{-1}$) when 4.7% nano-sized Fe_2O_3 powder is added to AP (Pang et al., 2010). The catalytic performance of nano-sized Co_3O_4 powder to the thermal decomposition of AP is obviously better than that of micro-sized Co_3O_4 particles. The exothermic peak of AP can disappear in the low-temperature region, the exothermic peak temperature in the high-temperature region dropped to 323.5°C, and the apparent thermal decomposition heat can be increased by 750 $J \cdot g^{-1}$, up to 1265 $J \cdot g^{-1}$ by nano-sized Co_3O_4 powder (DeLuca et al., 2009, 2010; Sinditskii et al., 2014). The decomposition peak temperature of AP in a high-temperature region can be dropped by 93°C, the thermal decomposition heat increased from 590 $J \cdot g^{-1}$ to 1490 $J \cdot g^{-1}$ by nano-sized NiO powder, and the catalytic activity of nano-sized NiO powder is better than that of micrio-sized particles (DeLuca et al., 2012). However, the overall performance (such as energetic, combustion, and hazardous properties) of composite solid rocket propellants containing nano-sized particles has barely been discussed in the open literature in detail so far. In our study, the characteristics of different nano-sized metallic oxide particles were analyzed by using scanning electron microscopy (SEM) and laser granulated analysis diagnostic techniques. Nano-sized particles were added to the formulations and five different propellant compositions with and without nano-sized powders were produced. The focus of this article is on how nano-sized metallic oxide particles affects the hazardous properties of composite solid propellant, placing emphasis on the investigation of the combustion properties, which could be used for solid rocket motor applications.

Experimental

Raw materials

Hydroxyl terminated polybutadiene (HTPB), plasticized with di-2-etylhexyl sebacate (DES, ≥99.4%), was cured with 2,4-toluene diisocyanate (TDI), and then micro-sized aluminum powders were used as components of the solid rocket propellant. Two types of ammonium perchlorate (AP) were utilized in the propellant formulation. The first consisted of pure research grade (>99% pure) ammonium perchlorate with an average particle size of 0.105–0.147 mm. The second type of ammonium perchlorate was made by grinding ammonium perchlorate (>99% pure) in a fluid energy mill to an average particle size of around 1–5 μm. Four different kinds of nano metal oxide particles (Fe_2O_3, Co_3O_4, CuO, and PbO) were used as components of composite solid rocket propellant. Except otherwise stated, all propellants were manufactured, processed, and tested at Xi'an Modern Chemistry Research Institute under identical conditions and using identical procedures.

The mass percentage amount of the ingredients used in the five different propellant formulations is as follows:

(1) CSP-1 (Reference Composition): HTPB/12.0%; Al/18.0%, AP/67.0%, additives/3.0%.
(2) CSP-2: HTPB/12.0%; Al/18.0%, AP/66.0%, Fe_2O_3/1.0%, additives/3.0%.
(3) CSP-3: HTPB/12.0%; Al/18.0%, AP/66.0%, Co_3O_4/1.0%, additives/3.0%.
(4) CSP-4: HTPB/12.0%; Al/18.0%, AP/66.0%, CuO/1.0%, additives/3.0%.
(5) CSP-5: HTPB/12.0%; Al/18.0%, AP/66.0%, PbO/1.0%, additives/3.0%.

The propellant formulations were mixed in 500-g batches using a 2-L vertical planetary mixer. All of the samples involved in this investigation were prepared by slurry cast technique at the temperature of 35°C and then solidified for 96 h (70°C) in a water-jacketed oven, were machined to a fixed dimension (shape: length, 100–150 mm; width, 2–5 cm; height, 2–5 cm).

Equipment and experimental details

SEM and particle size distribution experiments

The specific surface area measurement was computed from the nitrogen adsorption isotherm obtained by static volume oxidized measurement at liquid nitrogen boiling temperature (77 K) (Xu, 2003). Samples were out-gassed at 100°C for at least 4 h at absolute pressure less than 133.3 Pa. All measurements were carried out with a completely automated instrument (ASAP 2010, Micromeritics, USA), leading to the final value of the specific surface areas expressed in $m^2 \cdot g^{-1}$. Electron microscopy was used to study the shape, size, morphology, and defects of powders. The morphologies of metal fuel particles were examined by scanning electron microscopy. Granulometal oxidize analyses (particle size and size distribution) of metal samples were performed through laser scattering (Malvern Mastersizer 2000) using a dry dispersion unit. The quantity of material per test was about 0.07–0.10 g. Obscuration filtering was switched on and set to values within the range of 0.5–10% (Boggs, 1984; Maggi et al., 2010; Yuasa et al., 1997).

Rheological experiments

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.

Burning rate test

A fine metal wire (0.1 mm in diameter) was threaded through the top of the strand with an alternating 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 sealed chamber, which was filled with a nitrogen atmosphere (Yan et al., 2009).

The burning rate measurements of propellant samples were carried out as follows: When a propellant strand was ignited under the nitrogen gas purge conditions, the pressure in the strand burner increased due to the addition of the gaseous products. However, the pressure valve attached to the nitrogen gas supplier was regulated automatically to reduce the nitrogen gas flow rate in order to maintain the pressure constant. Thus, the pressure in the burner was maintained at the desired pressure. The burning rate

was measured by determining the instant of melting of five low-melting-point fuse wires of lead metal (5 mm in diameter) threaded through the strand at accurately known separation distances (140 mm). These five fuse wires, each in series with a resistor, form five parallel arms of an electrical circuit, whose output voltage changed discontinuously as soon as a fuse wire melted. The temperature of the strand could also be measured by a calibrated copper-constantan thermocouple threaded through the strand with the bead of the thermocouple placed in the center of the strand. The real time data was recorded by a computer, which processed and calculated the burning rate. Five replicate experiments were conducted at each test pressure and the average experimental results were obtained with a standard deviation of 0.13–0.25.

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 (Zhi et al., 2004) and results were given in terms of the statically obtained 50% probability of explosion (H_{50}). The friction sensitivity was measured with a Julius Peter apparatus (Ma et al., 2004) by incrementally increasing the load from 0.2 to 36 kg, until no ignition was noted in five consecutive test samples.

Heat of explosion test

The measured heat of combustion values were investigated by isothermal methods. A definite mass of propellant sample was put into the calorimetal oxidized oxygen bomb, which was surrounded by a fixed mass of water. The propellant was ignited in the bomb and the heat of explosion of the sample was calculated according to Eq. (1) as follows after the values of the elevated temperature of the water were measured (Ma et al., 2003):

$$Q_v = (C\Delta T - q_1)/m \tag{1}$$

where Q_v is the heat of explosion ($J{\cdot}g^{-1}$); C is the thermal capacity of the calorimeter ($J{\cdot}K^{-1}$); ΔT is the increased temperature value of the propellant during combustion (K); q_1 is the heat of explosion of initiation wire (J); and m is the mass of sample (g).

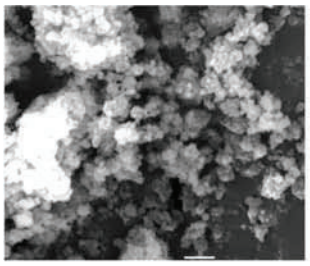
Density test

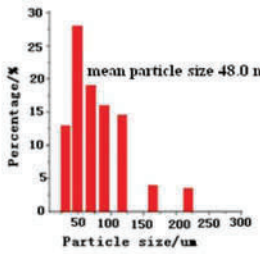
The density measurements of propellants were carried out with a Model AG 104 METTLER TOLEDO balance with rectangular-shaped samples of 30 mm × 30 mm × 10 mm, which were steeped in liquid paraffin at a temperature of (20 ± 2)°C.

Results and discussion

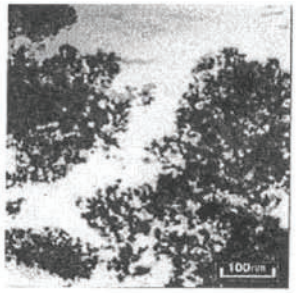
SEM and grain size distribution analysis

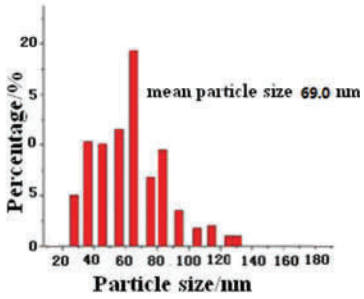
Detailed morphology information concerning the powder was collected by running a series of advanced diagnostic techniques, including scanning electron microscopy (SEM) and grain size distribution. Four types of well dried metal particles were free of fluid; the microstructures and grain size distributions are shown in Figure 1 and Table 1, respectively.



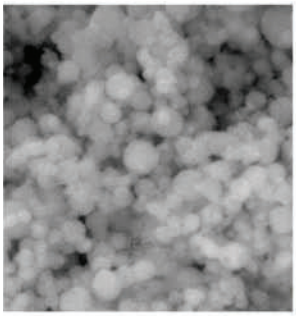


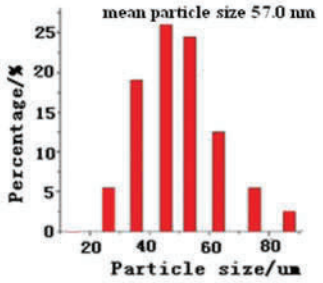
(a) Fe_2O_3



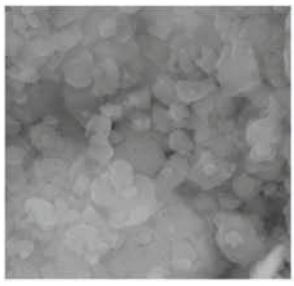


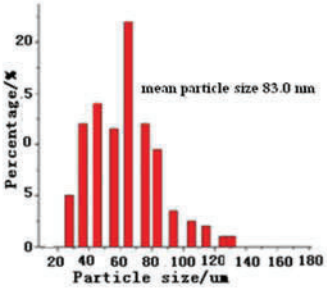
(b) Co_3O_4





(c) CuO





(d) PbO

Figure 1. SEM images and grain size distribution of the tested nano-sized metal oxidizer particles [high magnification (×500)].

Table 1. Characteristics of different nano-sized metal oxidizer particles.

Items	Unit	Fe_2O_3	Co_3O_4	CuO	PbO
d_{10}	μm	0.018	0.036	0.029	0.042
d_{50}	μm	0.048	0.069	0.057	0.083
d_{90}	μm	0.097	0.158	0.113	0.185
Span	—	1.646	1.768	1.474	1.723
Density	$Kg{\cdot}m^{-3}$ ($\times 10^3$)	5.24	2.24	6.31	9.53
Specific surface area	$m^2{\cdot}g^{-1}$	52.13	17.87	35.21	19.31

In the table, d_{10} is particle diameter corresponding to 10% of the cumulative undersize distribution (nm); d_{50} is median particle diameter (nm); d_{90} is particle diameter corresponding to 90% of the cumulative undersize distribution (nm); Span = $(d_{90}–d_{10})/d_{50}$; and the specific surface area refers to the particle size distribution determined with a Malvern Mastersizer.

It can be seen from Figure 1 and Table 1 that the microstructures of all tested powders present small particle size and nearly spherical shapes. The median diameters d_{50} of Fe_2O_3 powder is 48.0 nm, which is lower than that of the other nano-sized metal oxidizer particles (48.0–83.0 nm). Corresponding to the lower values of d_{50}, the specific surface area of Fe_2O_3 powder is 52.13 $m^2{\cdot}g^{-1}$, which is much larger than that of the other nano-sized metal oxidizer powders (17.87–35.21 $m^2{\cdot}g^{-1}$). Also, the width of different nano-sized metal oxidizer particles is in the range from 1.474 to 1.768, corresponding to their particle size distribution curves, which are much smoother.

Effects of different nano-sized metal oxidizer particles on the composite propellants slurries

The rheological properties (viscosity and yield stress) of different nano metal oxidizer particles in the HTPB binder plasticized with di-2-ethylhexyl sebacate were used to determine the characteristics of the preparation process for composite solid propellants. The propellant slurries were stirred effectively and kept in an oven at 50°C, and the rheological results of the propellant slurry in 1 h are shown in Table 2.

It can be found that the rheological properties of the propellant slurry show a behavior of pseudo-plastic, non-Newtonian fluids. Nano-sized metal oxidizer particles, when it was added in the composite solid propellant, can increase the viscosity of the slurry significantly. The viscosity and yield stress of the propellant slurries without nano-sized metal oxidizer particles (sample CSP-1) were slightly lower than those of propellant slurries containing nano-sized metal powder. This phenomenon attributes to the nano-sized particle effects on the processing performance and pot life of propellants.

Table 2. Effect of different nano-sized metal oxidizer particles on the rheological properties for composite propellants (shear rate: 1 s^{-1}).

Compositions	Viscosity (Pas)	Yield stress (Pa)	Flowing property of propellant slurry[a]
CSP-1	278.12	75.33	A
CSP-2	412.76	122.76	B
CSP-3	387.56	102.12	B
CSP-4	378.41	98.08	B
CSP-5	347.58	88.21	B

[a]Labels A–D denote the flowing property of propellant slurry from good to bad.

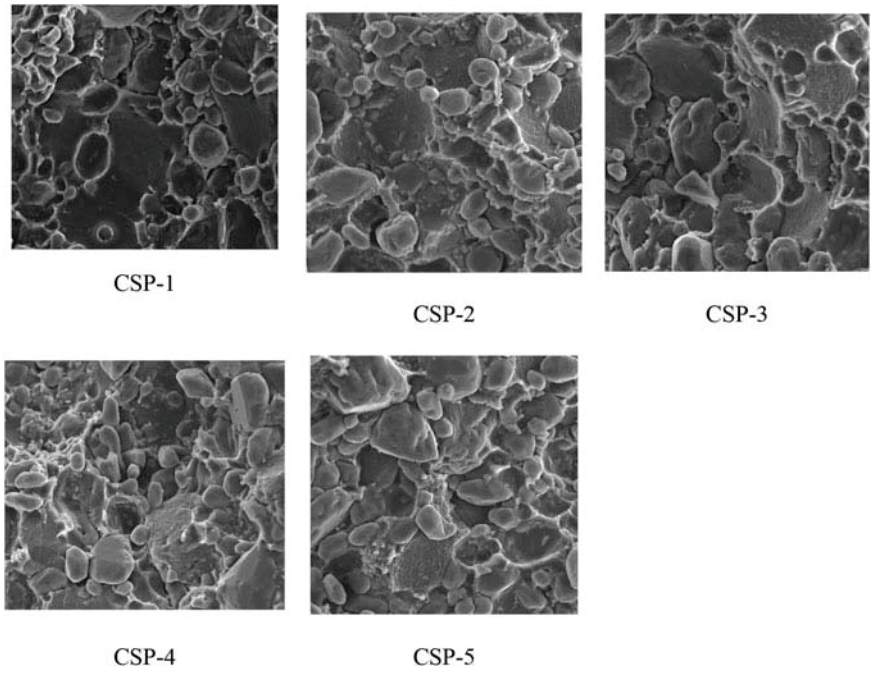


Figure 2. Microstructure surface of composite propellants containing different nano metal oxidizer particles [high magnification (×500)].

In order to analyze the physical structures of composite solid propellants containing different nano metal oxidizer particles, the microstructures of propellants with various particles are shown in Figure 2.

Figure 2 indicates that there are many granulated particles on the surface of cured composite propellants. The different nano-sized metal oxidizer particles are compatible with the ingredients of composite solid propellant systems, and the granulated particles with smaller diameters can fill into the spaces between the bigger grains sufficiently.

Properties of composite solid propellants

Energetic properties (density and heat of explosion)

Measurements of the densities and heat of explosion were conducted for each propellant. Table 3 summarizes the results of these tests.

Table 3. Effects of different nano-sized metal oxidizer particles on the energetic properties for composite propellants.

Compositions	Heat of explosion ($J \cdot g^{-1}$)	Density ($kg \cdot m^{-3}$ ($\times 10^3$))
CSP-1	6132	1.734
CSP-2	6068	1.767
CSP-3	5981	1.738
CSP-4	5926	1.768
CSP-5	5858	1.802

It can be seen from the results in Table 3 that the density of composite propellants with different nano-sized metal oxidizer particles is in the range of 1.738–1.810 g·cm^{-3}, which is much larger than that of the propellant without nano-sized powder (1.734 g·cm^{-3}). Increasing the high density materials and fine particle percentages leads to an increase in propellant density, which may be due to better powder packing during the manufacturing process. The heat of explosion of composite propellant CSP is 6132 J·g^{-1}, which is higher than those of propellant with nano-sized metal oxidizer particles (5858–6068 J·g^{-1}). The sequence of measured heat of explosion and density for the composite propellants with different metal fuels is as follows: [CSP-5] < [CSP-4] < [CSP-3] < [CSP-2] < [CSP-1], [CSP-1] < [CSP-3] < [CSP-2] < [CSP-4] < [CSP-5], respectively.

Hazardous properties

Metal particles, such as zirconium powder etc., are very friction sensitive. Thus, it is necessary to study the hazardous properties of propellants containing different nano-sized metal oxidizer particles. Results of the hazardous properties experiments are shown in Table 4.

It can be seen from the results in Table 4 that all of the propellant formulations containing various nano-sized metal oxidizer particles were sensitive to impact and friction except the reference sample without nano-sized powder, which is more insensitive to friction as compared to the other compositions. The sensitiveness may be attributed to the fact that there are mainly two major issues that determine the impact sensitivity: the molecular structure and the aggregation state. The latter case is possible for nano-sized particles, which increases the interfacial contacts resulting in higher porosity. Such porosity is responsible for hotspot generation. In the case of the data in Table 4, there is not much change on the impact and friction sensitivity, which may be attributed to the mass fraction of nano-sized metal oxide particles that is only 1% in the propellant formulation. The result reveals that the use of nano-sized powder in solid propellant leads to an increase in the sensitivities of friction and impact for the composite solid propellant, whereas its application in the propellants is feasible and safe.

Effects of different nano-sized metal oxidizer particles on the combustion characteristics of composite propellants

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. The burning rates described 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

Table 4. Hazardous properties of composite propellants with different nano metal oxidizer particles.

Compositions	Friction [P] (%)	Confidence level of 95% believed level	Impact [H_{50}] (N·m)	Standard deviation S (logarithmic value)
CSP-1	81	(55%, 91%)	7.29	0.10
CSP-2	92	(86%, 100%)	5.36	0.13
CSP-3	87	(81%, 98%)	5.57	0.23
CSP-4	86	(80%, 96%)	6.29	0.07
CSP-5	84	(69%, 98%)	6.92	0.15

could probably take place via two potential pathways (Hong et al., 2001; Li, 2008; Ma et al., 2004). 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 rates data of propellants containing different nano-sized metal oxidized particles obtained under different pressures are shown in Table 5 and Figure 3.

It can be seen in Figure 3 that all of the nano-sized metal oxidizer additives can affect the combustion behavior and change the burning rate when the other ingredients are the same. The burning rates of all propellants increase with increasing the pressure. The pressure exponent of CSP-1 formulation is 0.40 (1–15 MPa), which is the highest one compared to those of the others. The burning rates and pressure exponents barely change, which may be attributed to the negligible mass fraction of nano-sized particles addition to the propellant formulations. The nano-sized Fe_2O_3 powders have small-size

Table 5. Burning rate and pressure exponent results of composite propellant with different nano-sized particles.

	Burning rate, ($mm \cdot s^{-1}$)					
Compositions	1 MPa	4 MPa	7 MPa	10 MPa	12 MPa	15 MPa
CSP-1[a]	10.04	15.55	18.72	22.56	25.94	31.20
CSP-2	12.47	17.87	20.12	23.37	26.82	32.37
CSP-3	10.71	16.47	19.32	23.12	26.33	31.68
CSP-4	10.42	15.58	18.92	22.97	26.13	31.51
CSP-5	10.16	15.67	19.21	22.89	26.08	31.45
	Pressure exponents (n)[b] at different pressure ranges					
Compositions	1–4 MPa	4–7 MPa	7–10 MPa	10–12 MPa	12–15 MPa	1–15 MPa
CSP-1[a]	0.32	0.33	0.52	0.77	0.83	0.40
CSP-2	0.26	0.21	0.42	0.76	0.84	0.32
CSP-3	0.31	0.29	0.50	0.71	0.83	0.38
CSP-4	0.29	0.25	0.54	0.71	0.84	0.39
CSP-5	0.31	0.36	0.49	0.72	0.84	0.39

[a]Reference composition.
[b]Pressure exponent.

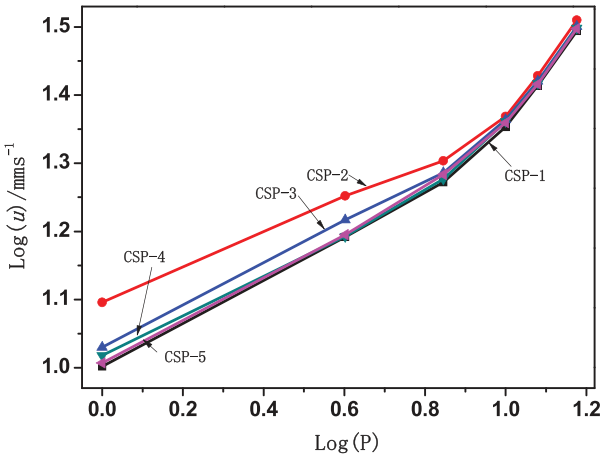


Figure 3. Burning rate of composite solid propellants containing different nano-sized metal oxidizer particles at different pressures (pressure range: 1–15 MPa; initial temperature: T_0 = 293 K).

effects; its promoting effect on the combustion of propellant is the main function in the experimental pressure range. The specific performances are as follows: (1) The ignition threshold of nano-sized Fe_2O_3 is lower than those of other nano-sized powders. (2) From the view of heat transfer, the addition of nano-sized Fe_2O_3 powder to the propellant can increase the heat adsorption in the combustion process effectively. From the view of dynamics, nano-sized Fe_2O_3 powder can contact with polymer binder and gaseous reactants because of their large specific surface area. Also, the releasing heats and heat transmission at the combustion surface for nano-sized Fe_2O_3 are higher than those of conventional ones at high pressure range. From the previous reports that the Co_3O_4 nano-sized particles (35 nm, –2% in AP) decrease the thermal decomposition of AP by 106.27°C, which is higher than that of CuO nano-sized particles (Yuan et al., 2003; Zhuang et al., 2001). It is known that, in the first exothermic decomposition step of AP, a solid decomposition reaction occurs to produce a large amount of N_2O, O_2,Cl_2, H_2O, HCl, and a small amount of NO (Bircomshaw and Newman, 1955; Boldyrev, 2006). There is a gas phase reaction to produce a large amount of NO, O_2, Cl_2, and H_2O etc. (Chen, 2006; Luo et al., 2001; Ma et al., 2000, 2004; Rosser et al., 1968). In the second exothermic decomposition step of AP, it is proved that oxygen species is preferably absorbed by the metallic species in catalytic processes as compared with CO, H_2O, etc., resulting in the following rapid reaction to form Fe_2O_3. It is also normally observed that the nano-sized metallic oxidizer particles are apt to burn or explode quickly as exposed to air. These rapid exothermic reactions may accelerate the decomposition of AP during the first stage. Following the above mechanism, apparently the enhancement effect of nano-sized metallic oxidizer particles depends on its content to provide the reaction heat.

Combustion flame morphology

To obtain a better knowledge of the effects of different nano-sized metal oxidize particles on the flame morphologies of the composite propellant, the combustion flame morphologies of composite propellants with different nano metal oxidizer particles at 1 MPa are shown in Figure 4.

It can be seen that the combustion flame morphologies of composite propellants with different nano-sized metal oxidizer 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 the aluminum metal particles to the propellant formulations. Although the metal oxidation process follows a common set of events, aggregation/agglomeration phenomena near the burning surface are notably different depending on the enforced operating conditions and details of the solid propellant formulation. Also, the luminosity of combustion flame morphologies for propellant containing nano-sized particles are magnified, which may be attributed to the small size of metal oxidizer powders in the compositions. Understanding of these effects opens a path to improved ballistic performance, which will be further investigated.

Conclusions

(1) The microstructures of tested powders present nearly spherical shapes. The median diameters d_{50} of nano-sized Fe_2O_3 powder is 48.0 nm, which is lower

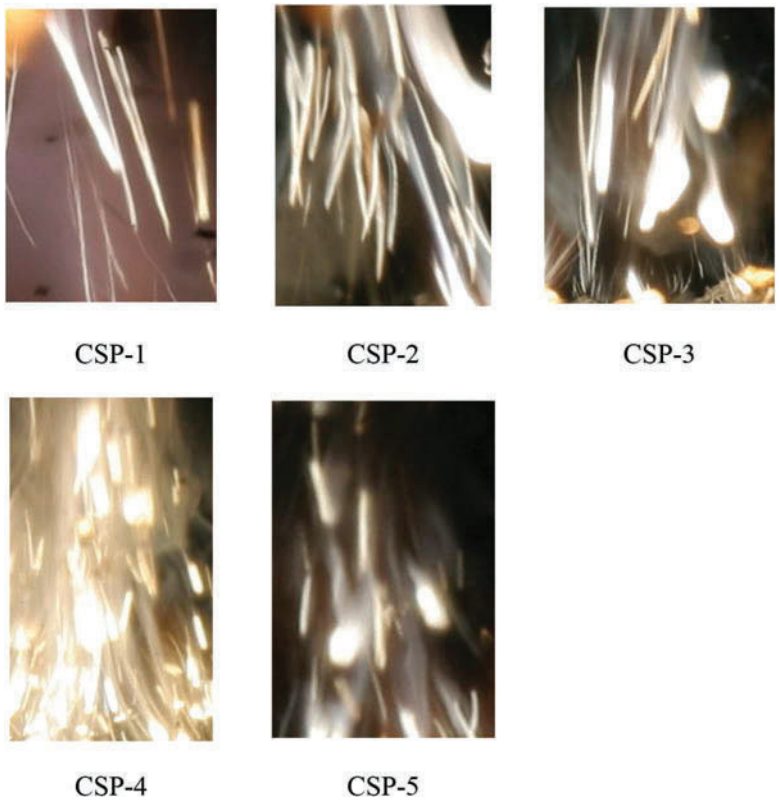


Figure 4. Combustion flame morphologies of composite solid propellants with different nano-sized particles (×500).

than that of the other nano metal oxidizer particles. Corresponding to the lower values of d_{50}, the specific surface area of Fe_2O_3 powder is much larger than that of the other nano-sized metal oxidizer powders. In addition, the width of different nano-sized metal oxidizer particles is in the range from 1.474 to 1.768.

(2) The tested different nano metal oxidizer particles are compatible with the ingredients of composite solid propellant systems, and propellants with nano-sized metal oxidizer can be prepared and cured by vacuum cast techniques. The granulated particles with smaller diameters can fill into the spaces between the bigger grains sufficiently.

(3) The tested composite propellants containing various nano-sized metal oxidizer particles feature increasing burning rate and density, but decreasing heat of explosion and pressure exponent (from 0.40 to 0.32 over 1–15 MPa) slightly with partial AP were placed by nano particles in the propellant formulation. Moreover, the hazardous properties (impact and friction sensitivity) of propellants with nano-sized metal oxidizers increase corresponding to the reference composition.

(4) The combustion flame morphologies of composite propellants with different nano metal oxidizer particles present multi-flame structures. Aggregation/

agglomeration phenomena near the burning surface are notable during the combustion process.

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Nomenclature

HTPB	hydroxyl terminated polybutadiene
AP	ammonium perchlorate
Al	aluminum powder
SEM	scanning electron microscope
d_{10}	particle diameter corresponding to 10% of the cumulative undersize distribution (μm)
d_{50}	median particle diameter (μm)
d_{90}	particle diameter corresponding to 90% of the cumulative undersize distribution (μm)
Span	$(d_{90} - d_{10})/d_{50}$
r	strand burning rate ($mm \cdot s^{-1}$)
a	pre-exponential factor of burning rate law
ρ	density ($g \cdot cm^{-3}$)
P	pressure (MPa)
n	pressure exponent

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