第 14 卷　第 6 期　　含　能　材　料　　Vol. 14, No. 6
2006 年 12 月　　CHINESE JOURNAL OF ENERGETIC MATERIALS　　December, 2006

文章编号: 1006-9941(2006)06-0471-04

Safe Preparations of Fine Ammonium Perchlorate Particles

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Abstract: Fine AP particles are required to manufacture the AP-based composite propellants with a wide burning rate range for various applications, especially high burning rate propellants. However, it is difficult to prepare a fine AP safely. Some safe methods for preparing the fine AP particles are reported such as the spray-dry method and freeze-dry method. It is shown that the crystal habit modified AP particle is an effective oxidizer to enhance the burning rate.

Key words: organic chemistry; ammonium perchlorate; fine particle; crystal habit; preparation; composite propellant

CLC number: TJ55　　**Document code:** A

1 Introduction

The ammonium perchlorate (AP)-based composite propellant is currently the most widely used one because this propellant has good burning characteristics and mechanical properties. One of the few serious drawbacks of the AP-based propellant is that its products of combustion, which include HCl, chlorine, and chlorine oxides, cause atmospheric pollution. Increasing concern for a clean atmosphere in recent years has resulted in a compelling need for developing a chlorine-free, environmentally friendly, smokeless propellant system. Various attempts made in this direction include the use of nitramines, such as HMX, RDX, ammonium nitrate, ammonium dinitramide, HNF, etc. instead of AP. However, the burning characteristics and rocket performance of these solid propellants are inferior to those of the AP-based propellant and a new solid propellant that can replace the AP-based propellant has not yet been found.

It is generally known that the burning rate of propellants increases with the decreasing mean diameter of the AP particles. The fine AP is required to obtain the high burning rate AP-based composite propellant. Fine AP can be prepared by a mechanical process such as grinding. A vibration ball mill is generally used as the grinding machine. It is difficult to prepare a fine AP, of which the particle diameter is less than 20 m, using a vibration ball mill[1,2]. Recently, a jet mill is typically used to prepare the fine AP. The jet mill is a dangerous apparatus for the preparation of fine AP because the fine AP is easily ignited and explodes by any slight impact or friction. When fine AP is prepared using a jet mill, it requires special modifications, such as an anti-explosive room, nitrogen atmosphere, impurity removal equipment, etc. It is not easy to safely prepare fine AP particles by grinding.

Klager[3], Hagihara[4,5], and Leu[6] reported the preparations of the coarse porous AP particles and these particles are the effective oxidizers to enhance the burning rate. These coarse porous AP particles were prepared by the thermal decomposition method. This method has many complicated processes and these particles could not be manufactured industrially. It had been not found the preparations of the fine AP particles. We reported that some safe methods for preparing the fine AP particles are the spray-dry[7-10] method and freeze-dry method[11-13]. The spray-dry method and freeze-dry method do not include any processes that produce on an impact and/or friction. Some safe preparations for the fine spherical, hollow, and porous AP particles will now be described. It was reported that the crystal habit modified AP particle is an effective oxidizer to enhance the burning rate[14]. It will be also described the preparations for the crystal habit modified AP particle.

2 Preparation by Spry-dry Method

A solution of AP is atomized by a two-fluid nozzle and the droplets are spayed into a drying chamber kept at high temperature. The droplets are dried and AP must be

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Received Date: 2006-08-07; **Revised Date:** 2006-09-05

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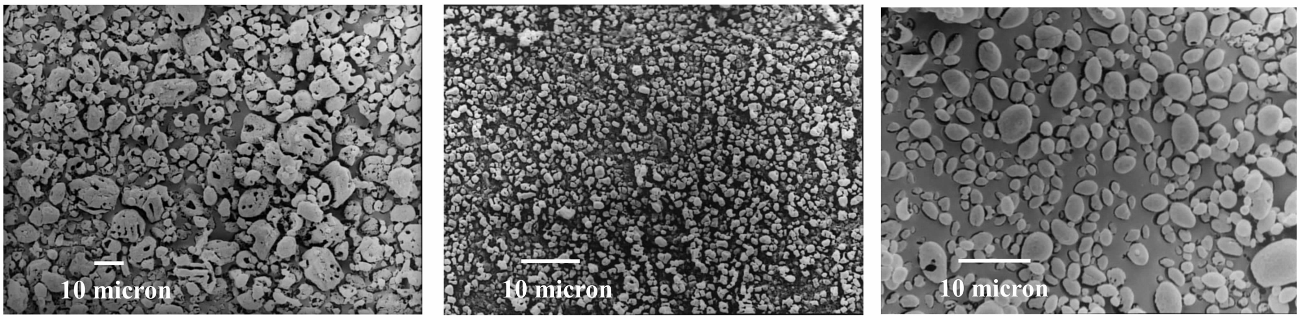
deposited as a solid phase when the surface concentration reaches the saturation value. The solid phase appears on the surface of the droplet as soon as the surface becomes saturated. After the formation of the shell on the droplet surface, the temperature of the solution inside the shell rapidly rises and the vapor pressure also quickly increases. Consequently, steam spurts out the droplet and the fine porous AP particles are prepared. Furthermore, the droplets are split by the steam egress. The particle size decreases with the increasing temperature in the drying chamber because the spurt of steam becomes stronger and the droplet is more split violently. When the inlet temperature of the drying chamber is in the range of 413 to 443 K, the porous AP particles with the mean particle diameter of 6.8 - 3.4 μm and the specific surface area of 1.0 - 2.1 $m^2 \cdot g^{-1}$ are prepared[7,8].

When the AP solution dissolved in an organic solvent, i. e., methanol, ethanol, and acetone, are spry-dried, the spurt of stream becomes stronger and the droplets are split more aggressively by the steam. Therefore, the finer porous AP particles are prepared, compared to that spray-dried with the AP solution alone and, furthermore, the fine spherical AP is also prepared. When the inlet temperature of the drying chamber is in the range of 313 to 413 K, the porous and spherical AP particles with the mean particle diameter of 1.3 - 2.4 μm and the specific surface area of 1.6 - 2.1 $m^2 \cdot g^{-1}$ are prepared[9].

The AP solution is atomized by an ultrasonic atomizer and the droplets flow into a drying chamber kept at the low temperature of 313 K. The steam only slightly spurts out of the droplet because the temperature of the solution inside the shell very slowly increases. Consequently, fine hollow AP particles are prepared. When the inlet temperature of the drying chamber is in the range of 313 to 413 K, the porous and spherical AP particles with the mean particle diameter of 2.7 - 2.9 μm and the specific surface area of 2.6 - 3.1 $m^2 \cdot kg^{-1}$ are prepared[10].

Figure 1 shows three fine AP particles prepared by the spray-dry method. References [7 - 10] describe the detail preparations of these spray-dried APs.



porous AP(mean particle diameter:3.5 μm) spherical AP(mean particle diameter:1.3 μm) hollow AP(mean particle diameter:2.7 μm)

Fig. 1 SEM photographs of spray-dried APs

3 Preparation by Freeze-dry Method

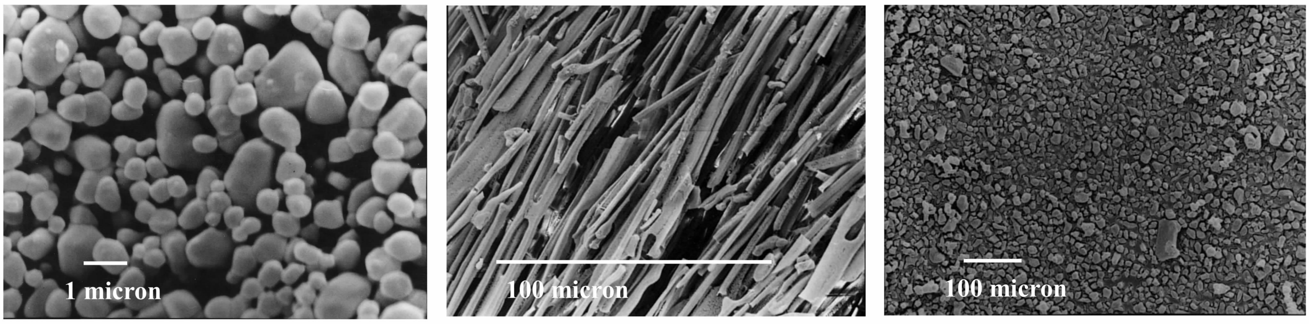
The AP solution is sprayed into liquid nitrogen by an ultrasonic atomizer. The frozen product is subsequently transferred to a freeze-dryer, and dried without melting. The fine spherical APs with the mean particle diameter of 1 μm were prepared by this method[11].

The AP solution is poured into a glass vessel, and the vessel is maintained under the reduced pressure. When the pressure in the vessel was decreased toless than 13 Pa, the solution is frozen. Most of the water in the frozen AP solution has been sublimated. Based on this phenomenon it is thought that this method is a type of freeze-dry method. The freeze-dried AP has a needle-like shape with a diameter of about 2 - 5 μm and the length of the needle-like AP is not constant[12].

The O/W emulsion is prepared by emulsifying with an organic solvent as the dispersed phase and AP solution as the dispersion medium. The organic solvents barely dissolve AP and water. The emulsion is frozen with liquid nitrogen, and the frozen emulsion was then freeze-dried. The fine AP is prepared by this method. The interfacial tension between the organic solvent and AP solution is correlated with the mean particle diameter of the prepared

AP. The mean particle diameter of the prepared AP decreases with the decreasing interfacial tension. The fine AP particles with the mean particle diameter of 4 – 11 μm and the specific surface area of 0.7 – 1.4 $m^2 \cdot g^{-1}$ are prepared[13]. Furthermore, the fine AP particles with the mean particle diameter of approximately 1 μm are prepared by the surface-active agents.

Figure 2 shows three fine AP particles prepared by the freeze-dry method. References [11 – 13] describe the detailed preparations of these freeze-dried APs.



spherical AP (mean particle diameter: 1 μm) needle-like AP spherical AP (mean particle diameter: 4 μm)

Fig. 2 SEM photographs of freeze-dried APs

4 Preparation of Crystal Habit Modified AP

The use of a crystal habit modified AP as an oxidizer is an effective technique to obtain a high burning rate composite propellant[14]. Its preparation is as follows: the saturated AP aqueous solution at 333 K is poured into an organic solvent such as ethanol, butanol, hexane, etc., cooled to 273 – 275 K. In the cooled mixture of the saturated AP aqueous solution and the organic solvent, the AP is rapidly crystallized. The crystal habit of the recrystallized AP is modified. Figure 3 shows an example of the crystal habit modified AP. Reference [15] shows the detailed preparations of the crystal habit modified APs.

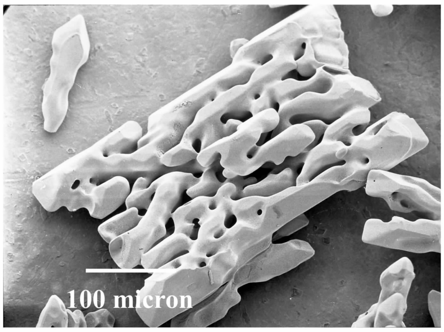


Fig. 3 SEM photograph of crystal habit modified AP

The specific impulse of the AP-based propellant increases with the increasing AP content. The upper limit content of the AP incorporated in the propellant exists due to the requirements for the preparation of the AP/HTPB composite propellant[8,16]. This indicates that an upper limit of the specific impulse must also exist. The upper limit of the AP content decreases as the size of the AP particle decreases[16]. Ultra-fine AP particles are undesirable for a high performance propellant because the propellant with a high AP content cannot be prepared.

Recently, many namometer-scaled metallic materials have been prepared using nanotechnology techniques and some attempts have been made to develop fine high energetic materials. It can be predicted that the burning rate and detonation velocity will be increased using fine energetic materials due to the increase in the reaction surface area. Metals are incorporated into propellants and fuel compositions primarily due to their high energy and energy density. Nanosize metal powders may be good candidates as fuel components because of their high reactivity due to their large reaction surface. However, most of the fine energetic materials are dangerous and the bulk density of the propellant and the explosive is decreased when using fine energetic materials and, consequently, the energetic performance is reduced.

It is necessary to prepare high energetic materials with various particle properties according to the required performance. The propellants with a wide burning rate range are required for various applications. It is necessary to develop a safe preparation of the oxidizer with various particle properties.

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（上接470页）

Progress in High Energetic Explosive: TEX

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Abstract: A high energetic explosive compound, 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX) synthesized by different routes is reviewed. The properties of TEX, such as explosive performance, thermal decomposition, friction sensitivity and impact sensitivity are summarized. It can be concluded that energy lever of TEX is higher than RDX, even exceeds TATB. Moreover, TEX is high solids pressable, extrudable explosive or simple castale explosive. It is expected that TEX has good potential applications in high performance, low sensitivity explosives.

Key words: organic chemistry; 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX); insentive explosive; review

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更 正

本刊2006年第5期第355页图1的第二步反应条件中$NaNO_2$，应为NaN_3；第385页中文摘要中"……释出的气体产物主要有：NO、N_2O、HCN、NO……"，应为"……释放出的气体产物主要有：NO_2、N_2O、HCN、NO……"。特此说明。

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