Preparation Progress of micro/nano-energetic materials

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Abstract. micro/nano-energetic materials(NEM) have been highly attended by many researchers for improved performance in terms of safety, energy release, ignition, and mechanical properties. Multifarious preparation techniques and methods have been developed, solvent- nonsolvent crystallization method is an important route, this article reviews the recent progress of NEM preparation research through solvent- nonsolvent crystallization method, various factors for affecting NEM size and shape are provided, such as mixed mode, solvent, liquid concentration and crystallization temperature, anti-aggregation measures.

1. Introduction

Micro/nano-energetic materials(NEM) are generally referred to as the energetic materials or energetic composites with at least one dimension size is in 100nm. Some researchers also classed the energetic materials with hundreds nanometer as NEM. NEM have the characteristics of small particle size, large specific surface area, high surface energy and strong surface activity[1], so its performances are improved and advanced compared with that of ordinary size energetic materials. For example, NEM can reduce the impact mechanical sensitivity, enhance the short pulse sensitivity, accelerate reaction rate or burning rate, and also decrease the detonation and combustion reaction spread critical dimension[2-10], see Table 1[3].

| Explosive | Particle size | Impact sensitivity(J) | Friction sensitivity (50% load,N) | Electrostatic sensitivity(initiation,J) |
|-----------|---------------|------------------------|----------------------------------|---------------------------------------|
| HMX       | Micro(few microns) | 6.2                    | 116                              | 0.25                                  |
|           | Submicro(<1µm)   | 6.6                    | 156                              | 0.62                                  |
| CL-20     | 15µm           | 5.0                    | 64                               | 45                                    |
|           | 1µm            | 8.0                    | No reaction                      | 49                                    |
|           | 95nm           | 11.0                   | No reaction                      | 60                                    |
| K-6       | micro          | 12.5                   | 64                               | -                                     |
|           | nano           | 15.0                   | 120                              | -                                     |

These changes can improve the ammunition’s safety, the energy output level and damage ability, so NEM have important significance to enhance the weapon system’s safety, reliability, multifunction and intelligent level. Micro and nano energetic materials have been widely used in new functional
components, and many researchers are interested in NEM’s preparation technology. United States, Russia, Iran, India and many other countries have invested lots of finance and human resources in this field.

However, energetic materials are much sensitive to heat, impact, friction and other external stimulation, many of other nanomaterials’ preparation methods cannot be used or directly used for NEM preparation, it is very significant to develop appropriate or new NEM preparation method. According to micro/nano particles different formation pathways, NEM can be prepared by initial discrete breaking method (i.e. from big to small method or top-down approach) or coagulation crystallization method (i.e. from small to big method or bottom-up approach). Discrete breaking method is the micro/nano method that continuously micronizes and disperses the common energetic particles by means of external fragmentation action or micro processing. The usual discrete methods are mechanical grinding, milling, high fluid crushing, ultrasonic crushing, etc., some of them are still widely used now. Coagulation crystallization method is one that transforms the energetic materials from liquid or gaseous atomic and molecular state into solid particles through nucleation and crystalline growth process. Discrete method has some shortcomings, for example, impurity can easily be brought into the objective product, and the fined degree is often limited, some nanostructure also cannot be obtained. So coagulation methods represented with chemical crystallization process have been attracted much attention.

Coagulation methods mainly include liquid phase crystallization method, vapor condensation method and sol-gel method. Liquid phase crystallization method can be subdivided into solvent/nonsolvent crystallization method(solvent/nonsolvent method), spray crystallization method and supercritical fluid crystallization method, etc. In these methods, solvent/nonsolvent method has some advantages over the others, such as simple crystallization principle, easy process control, low cost, wet state and low temperature operating. For some energetic materials, nanoparticles or nanostructure(nano-network, nanowires, nanotubes) can also be obtained under optimum conditions, leading this preparation method’s study becoming deeply and systematically, many NEM used for slapper detonator and other explosive devices have been prepared by this method. This paper is a brief review about the NEM preparation through solvent/nonsolvent method.

2. Research development and influence factors
The theoretical basis of solvent/nonsolvent method for preparing NEM is the liquid phase crystallization theory, namely, under certain pressure and temperature conditions, the solution has three states and three regions due to different concentrations: unsaturated state, saturated state, supersaturated state and stable region, metastable region and unstable region. When energetic material solution exists in the supersaturated state and unstable zone, the solute will nucleate and then grow, finally become crystals or particles.

The key of preparing NEM with solvent/nonsolvent method is mixing energetic material solution(liquid) and nonsolvent or poor solvent(generally called nonsolvent) quickly and strongly under certain conditions, which makes the solution reach supersaturation state and nucleate quickly in a very short time. By controlling the process of crystal nuclei formation and growth, inhibiting the growth speed of crystal nuclei, nano scale energetic particles can be prepared.

During NEM preparation, there are many factors determining NEM particle size, morphology and other structure parameters. These factors are mixed mode, liquid concentration and temperature, anti-aggregation measures, etc.

2.1 Mixed mode
There are three modes for liquid and nonsolvent mixing: positive feeding mode, reverse feeding mode and impact mixed mode. Mixed mode is an important factor which affects micro/nano products’ particle size and morphology, this effect is showed in fig.1.
2.1.1 Positive feeding mode
Under positive feeding mode, the supersaturation of early crystallization stage is rather low, lots of nucleation cannot be formed in a short time, and the nucleation number is limited. So the obtained particle size is large, size distribution is wide and surface area is low. For example, when PETN explosive was fined by positive feeding mode, the obtained particle size is tens of microns or hundreds of microns\(^{[15]}\). Therefore, positive feeding mode is seldom used in practice.

2.1.2 Reverse feeding mode
The main characteristic of reverse feeding mode is energetic materials solute nucleates and crystallizes in lot of nonsolvent, so small amount of liquid contacts with lot of nonsolvent, making the solution reaches high supersaturated state, energetic solute instantly precipitates, thus a large number of small nuclei are formed. Strong actions like high speed stirring make the precipitated tiny energetic particles well dispersed, particle growth process is inhibited as well, so nanoscale energetic particles can be easily produced. Reverse feeding mode has been widely used in NEM preparation, many researchers have used this method to prepare micro/nano HMX, TATB, BTF, PETN, HNS, NTO, RDX, LLM-105, CL-20 and other energetic materials\(^{[16-25]}\).

Under reverse feeding mode, liquid can be dropped to the nonsolvent by dropping device or sprayed into nonsolvent by special structure device. The approach of liquid enters into nonsolvent has a significant effect on the solution droplet size and supersaturation of micro mixing region, then greatly affects the particle size and size distribution. When small droplets are mixed with nonsolvent, the droplets can be quickly dispersed to a wide range of crystallization system, the environments of each micro crystalline region are similar, so the speed of nucleation and growth. Those tend to get micro/nano particles with a narrow range of particle size distribution.

2.1.3 Impact mixed mode
In impact mixed crystallization process, nonsolvent and energetic material solution will form two high speed and high strength jets with small diameter, high pressure after pressed. Then two jets are mixed with appropriate way, solute crystallize quickly resulting in fine particles. The high-speed impact process can be regarded as a kind of special crystallization process which high-speed turbulent mixes along with strong shear disperses. The liquid is sheared into almost Kolmogorov scale micelles by nonsolvent jet of massive high-speed movement. Therefore, it can also be considered a microcluster dynamic crystallization process.

Under high velocity impact, the supersaturation of microcluster crystallization region changes greatly, microcluster’s mixing state is very uniform. Both nucleation and growth process are completed in a very short period of time, solute nucleate largely and uniformly. In strong turbulent environment produced by high-speed jet, the obtained micro/nano particles are quickly dispersed to large quantities of nonsolvent liquid, making it is difficult to sustain crystal particle growth, then crystal agglomeration process is restrained effectively. Strong jet and agitation also promote nano
energetic particles well dispersed, reduce the particles agglomeration and is helpful to obtain energetic particles with micro/nano scale and narrow particle size distribution. This mode also has been widely used in preparation of many NEM as TATB, HNS, RDX, CL-20, NTO, etc\textsuperscript{[26-30]}.

2.2 Liquid concentration and temperature
Liquid concentration is an important factor to form supersaturation. Generally, high supersaturation requires high liquid concentration. However, excessive concentration will influence the micro crystalline region uniformity, which results in affecting the product particle size and distribution, the supersaturation should be controlled in a proper range. For example, using DMF as solvent and non-ion surfactant OP-10 as anti-agglomeration agent to prepare micro/nano RDX, the particle size and morphology of obtained micro/nano RDX are different under different liquid concentrations\textsuperscript{[29]}, see Fig.2.

![Fig.2 The effect of liquid concentration on the shape and particle size of ultrafine RDX](image)

When using concentrated sulfuric acid, DMSO and other high viscosity liquid as solvent, the liquid concentration has a different effect on the micro/nano degree compared with low viscosity solvent, i.e. lower liquid concentration is easy to the liquid’s spread and has a more nuclear number, then obtaining a smaller particle size\textsuperscript{[25]}.

Crystallization temperature also significantly affects the supersaturation of crystallization system, solute nucleation and growth speed, then affects the NEM’ particle state (aggregation or dispersion), particle diameter, particle size distribution and specific surface area. Higher supersaturation has stronger nucleation driving force, so lower temperature is helpful to promote solute nucleate in short time, and nano particles agglomerate more slowly under lower temperature. So the gotten energetic material has a higher specific surface area, smaller particle size and narrower particle size distribution. Therefore, low temperature crystallization is usually used during NEM preparation\textsuperscript{[25-30,29]}.

![Fig.3 The effect of crystallization temperature on the shape and particle size of ultrafine RDX\textsuperscript{[29]}](image)

2.3 Anti-aggregation measures
Nano energetic particles are unstable and easy to agglomerate for their high surface energy, thus anti-aggregation measures must be used during NEM preparation process. There are several nano energetic particle agglomeration mechanisms, such as capillary adsorption, hydrogen bonding and crystal bridge, etc\textsuperscript{[1]}. For example, surfactant is an effective way to prevent agglomeration. Many
researches show that when surfactant exists in crystallization system, the surfactant can be adsorbed on small particles surface and forms a thin coating layer. This coating layer can hinder the fine particles close to each other and reunion, also hinder the energetic component of solution close to nano energetic particles, thus surfactant can both inhibit particles agglomeration and growth. Therefore, NEM particle size can be regulated by adding surfactant[25], see table2.

| Dose of surfactant / % | Specific surface area / m².g⁻¹ | D₅₀/ nm | Peak value size/nm |
|------------------------|---------------------------------|---------|--------------------|
| 0                      | 5.2                             | 2716    | 3687               |
| 3                      | 31.5                            | 107     | 107                |

Vigorous mixing is another way to prevent aggregation. Vigorous mixing in the solvent/non-solvent crystallization process can make liquid and non-solvent reach to supersaturation and uniform state once they contact. Also, the environment of micro crystalline region is very similar, which goes for solute’s coincident nucleation and growth process. Due to the factors above, it is easy to get nano energetic particles with uniform particle size and narrow particle size distribution. In addition, strong colliding and shearing actions provided by high intensity mixing are also helpful for broken and scattered of NEM particle aggregates. What’s more, the precipitated small particles are difficult to agglomerate. So NEM particles with high specific surface area and small particle size can be obtained under strong mixing[23-27].

2.4 Other factors

Solvent has an obvious influence on NEM particle size and morphology, which is mainly due to the solvent viscosity and the diffusion speed of liquid in nonsolvent. For example, using acetone as solvent, it can get superfine RDX particles with near morphology and size, but the obtained small particles are easy to adhere to large particles; taking the mixture of acetone and DMSO as solvent, obtained ultrafine RDX particle has a uneven size distribution and diverse particle morphology, see fig.4[29].

![Fig.4: The effect of solvent system on the shape and particle size of micro/nano RDX](image)

Ultrasonic wave has the function of breaking and dispersion, applying ultrasound field to NEM preparation process, liquid medium will produce a large number of micro bubbles under the action of ultrasonic field. Micro bubbles’ collapse can induce a large number of solute nucleation and also disperse fine particles aggregate. Therefore, ultrasound field is beneficial to nanoscale energetic particle production and particle size distribution control[31-34]. For example, applying ultrasonic wave to NEM’s solvent/non-solvent preparation process, the obtained nano HNS powder has an average particle diameter of less than 360 nm and specific surface area of more than 23m²/g[31]. The obtained nano HMX has an average particle diameter of about 100nm[34] and nano CL-20 has an average particle diameter of 95nm and ellipsoidal shapes[33].

By optimizing these factors, the solute can nucleate largely and homogeneously, the grain growth can be inhibited and micro/nano effect is improved. So this method can prepare micro/nano TATB.
product with specific surface area of 38m²/g and grain degree of 41nm\textsuperscript{[27]}. Also it can obtain different structure of NEMs, such as long strips and loose nano TATB, granular micro/nano HNS, tubular structure of micro/nano BTF. Surfactant is an important factor to affect NEMs particle morphology, when preparing micro/nano HNS through two fluid nozzle impact crystallization device, the obtained HNS particles is 300nm and short block if no crystal habit adjustment agent, while the particle shape will be long block in the presence of sodium carboxymethyl cellulose\textsuperscript{[20]}.

3. Conclusion
Solvent/nonsolvent crystallization method has the advantages of safety, nano level, scale production and so on. It has good prospect for practical application and has become the key method of NEM preparation. This article reviews the progress of NEM preparation through solvent/nonsolvent method and discusses the main factors which affect the product particle size and morphology.

The main research directions in the future is combining solvent/nonsolvent crystallization method with other new technology as self-assembly and 3D printing technology, this can prepare various more structured and functional NEM, i.e. nano network, nano flake, nanowire, micron tubular or other nanostructures.

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