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Microstructure and Fractal Characteristics of Superfine TATB and HNS

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Abstract: Two superfine particles of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), 2,2′,4,4′,6,6′-hexanitrostilbene(HNS) were prepared respectively and their particle conglomeration's microstructures were studied by SEM method, gas sorption method, and fractal method. Results show that the HNS conglomeration consists of cashew-like nanometer crystals which piles up tightly here or loose somewhere else with surface area of 11.8 $m^2 \cdot g^{-1}$, and the TATB conglomeration consists of nanometer crystals which connect mutually with surface area of 24.77 $m^2 \cdot g^{-1}$. Both samples show IV type desorption isotherms with hysteresis loop ranged in high relative pressure 0.8–1. Barrett-Joyner-Halenda (BJH) analysis and Horvaih-Kawazoe (HK) analysis indicates that TATB conglomeration has the higher pore volume and higher surface area than HNS conglomeration before 12 Å and after 80 Å, while it is reverse within 12–80Å, which indicate that the microspore contributes to pore volume more than mesopores. In addition, the fractal microstructure are found from the desorption isotherm of both samples. The fractal dimension behaves low in range of relative pressure p/p_0 of 0.00–0.04, medium in 0.04–0.10, and high in 0.1–0.2. TATB conglomeration has higher fractal dimension than HNS in every similar range. BJH data, HK data, and fractal analysis disclose more details of microstructure than surface area and the textual discussion should be expected beneficial to comprehension of microstructure and microstructure - performance relationship.

Key words: superfine explosives; HNS (2,2′,4,4′,6,6′-hexanitrostilbene); TATB(1,3,5-triamino-2,4,6-trinitrobenzene); microstructure; conglomeration; isotherm; fractal analysis
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1 Introduction

Superfine particles of explosives were researched for decades in order to obtain explosives with lower sensitivity and ameliorative initiating performances. Early investigations focused on the reduction of particle size and regulation of initiating performance[1-3]. Common methods included grinding of coarse particles and recrystallization of nanometer particles. The fresh-formed superfine particles owned really high surface energy and their aggregation were progressed within manufacture and application, which prohibited partially the advantage of superfine particles and counteracted the amelioration of initiating performances. Aggregation and anti-aggregation of superfine particles was confirmed vital gradually. In order to characterize the aggregation and its effects on the initiating performances, particle size is no longer the exclusive parameter and surface area becomes the more practical parameter in quality control[4]. Surface area could impossibly disclose the all of the actual microstructure of superfine particles and their conglomeration, and more details were expected for profound comprehension.

Fractal analysis, widely used in many areas of modern science[5], was introduced into explosives researches. Fractal phenomena were discovered early within the framing photographs of explosive samples under drop-hammer test[6-8], the fractal dimension was related to the impact sensitivity, and the sequential order of fractal dimension was in agreement with that of the drop hammer height for the six experimental explosives. Fractal phenomena were then found within the complicated surface of TATB- binder particles under AFM (atomic force microscopy) in situ heating observation[9] which might be relevant to activation and crystallization of binder. Fractal characteristics of molecular-crystal structure of TATB explosive were found relative to their manufacture method[10]. Fractal analysis was found feasible within particle size distribution and morphological measurements of HMX, RDX, and PBX9501 explosives[11].

Fractal phenomena were also found in our experiments of grinding of BNCP (tetraammine-bis-(5-nitro-2*H*-tetrazolato-N2) cobalt (Ⅲ)-perchlorate) explosive[12]. Fractal dimensions of particle size distribution of particles increased during grinding and did not increase any longer when mean particles size decreased to less than ten micron. It was deemed that quantity of submicron and nanometer particles should aggregate and formed lower density conglomeration which introduced abnormality into fractal dimension calculation assumption. In other words, fractal dimension could be relative to decrease of particle size and aggregation of superfine particles.

In the context, microstructure of TATB and HNS superfine explosives was studied including the aggregation of nanometer crystals, the desorption isotherms of both conglomeration samples, their fractal characteristics, and etc.

2 Experimental

2.1 Preparation of Superfine Particles and Conglomeration Samples

HNS superfine particles were prepared according to literature [2]. Hot HNS/DMF(dimethyl formamide) solution were sprayed rapidly into cryogenic deionized water to promote nucleation and prohibit nucleus growth so that majority of HNS precipitated with submicron and nanometer size. These superfine particles aggregated to form conglomeration sample during

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washing with quantity of deionized water and dehydrating under room temperature.

TATB superfine particles were prepared similarly according to solvent-nonsolvent recrystallization method[3]. Hot TATB/concentrated sulfuric acid solution was sprayed rapidly into cryogenic deionized water and majority of TATB precipitated with submicron and nanometer size. These superfine particles aggregated to form conglomeration sample during washing with quantity of deionized water and dehydrating within vacuum freeze-drying machine.

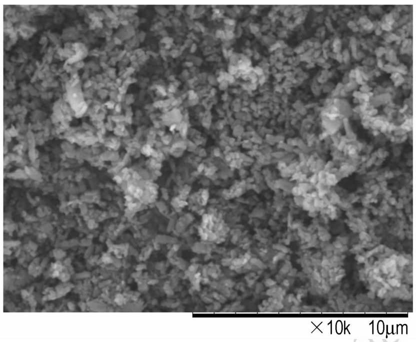
2.2 Morphology and Microstructure Analysis

The surface morphology of the conglomeration samples were measured with TM1000 scanning electron microscope. The microstructures data of the conglomeration samples were measured with Quantachrome nova automated gas sorption system.

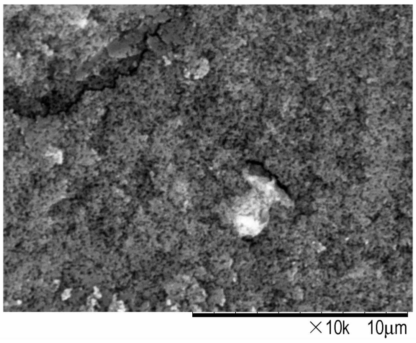
3 Results and Discussion

3.1 Morphology and Surface Area

The conglomeration sample was observed to consist of nanometer crystals as given in Fig. 1. HNS conglomeration sample consisted of cashew-like nanometer crystals with their length less than 1 μm, their diameter round several hundred nanometers, and length-diameter ratio round 3 : 1 – 4 : 1. These nanometer crystals piled up tightly here or loose somewhere else to form the conglomeration sample. TATB conglomeration sample consisted of nanometer crystals with their length and diameter smaller than that of HNS. These TATB crystals connected mutually to form framework-like conglomeration as in literature [13].



a. HNS



b. TATB

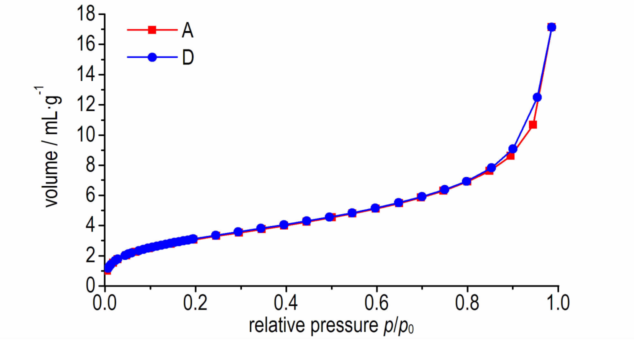
Fig. 1 SEM micrograph of conglomeration sample of HNS and TATB

HNS conglomeration were measured up to $11.8\ m^2 \cdot g^{-1}$ (correlation coefficient 0.99966) which was close to literature[14–15]. TATB conglomeration were measured up to $24.77\ m^2 \cdot g^{-1}$ (correlation coefficient 0.99987). It was in accordance that TATB conglomeration sample consisted of smaller crystals and owned higher surface area than HNS did. Besides, application of freeze-dryer dehydration within manufacture of TATB sample would prohibit aggregation of nanometer crystals better than room temperature dehydration within manufacture of HNS sample.

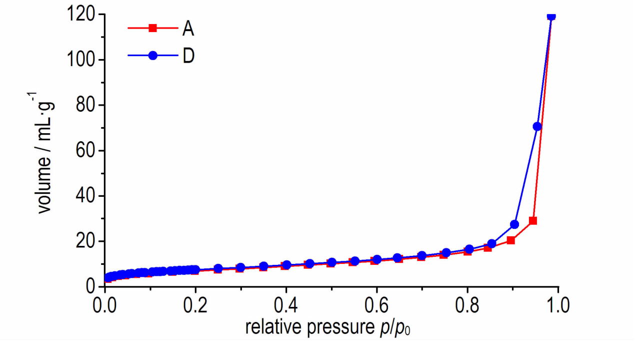
The surface area of conglomeration sample was assumed vital to sensitivity of explosives[16] and higher surface area should be obtained with milder aggregation under more skilled manipulation and milder aggregation within recrystallization, washing and dehydration. After all, aggregation should be only prohibited and not avoided entirely.

3.2 Desorption Isotherm and Fractal Analysis

Both the two conglomeration samples showed IV type desorption isotherms as given in Fig. 2. HNS sample showed smaller hysteresis loop within range of high relative pressure (p/p_0) 0.8 – 1 and TATB sample showed bigger hysteresis loop with slimly wider relative pressure range 0.7 – 1. The difference between two isotherms was in accordance with their preparation techniques: freeze-dryer dehydration within TATB preparation might prohibit collapse of space between nanocrystals more effectively during sublimation of moisture and led to more porous microstructures than room temperature dehydration within HNS preparation.



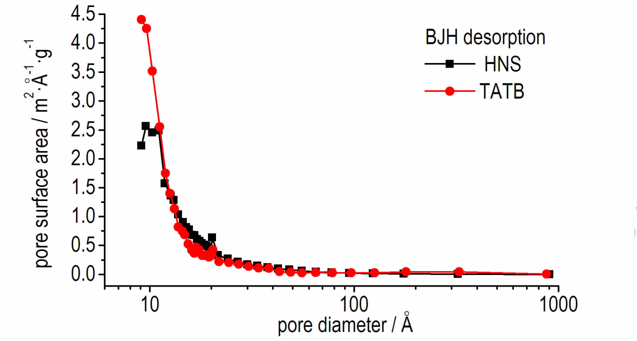
a. HNS



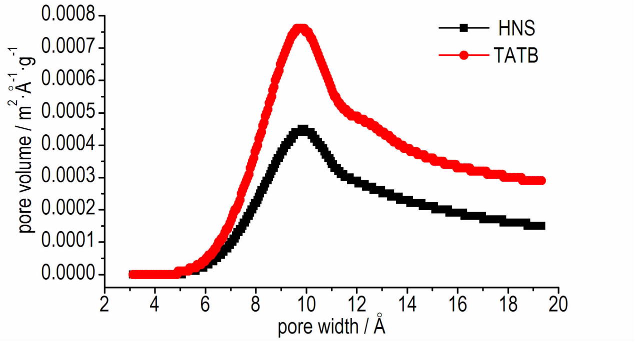
b. TATB

Fig. 2 Desorption curves of conglomeration sample

Barrett-Joyner-Halenda (BJH) and Horvaih-Kawazoe (HK) desorption curves of the conglomeration samples was given in Fig. 3 with approximately similar profile. BJH curves of TATB sample showed higher pore volume and higher surface area before 12 Å and after 80 Å than that of HNS, while it was reverse within range of 12–80 Å. It was obvious that total surface area from BET methods should be in accordance with not details but the integration of isotherm. BJH and HK desorption curves also showed that micropores contributed to pore volume more than mesopores.



a. BJH



b. HK

Fig. 3 BJH and HK curves of two conglomeration samples

Microstructures of conglomeration samples were analyzed with fractal analysis. Fractal dimension was calculated according to desorption curve in Fig. 2 and Avnir-Jaroniec method[17] as followed:

$$\ln(n)=\mathrm{const}-(3-D)\ln(A) \qquad (1)$$

$$A=-RT\ln(p/p_0) \qquad (2)$$

where D is the value of fractal dimension, n is molar amount of adsorbate adsorbed at the relative pressure p/p_0 and absolute temperature T (K), R is equal to 8.314 Pa · m^3 · mol^{-1} · K^{-1} and A is the so-called adsorption potential defined as in formula (2).

The ln(n)-ln(A) fitted beeline very well with high correlation coefficients within p/p_0 range of 0.005–0.2 and the slope of beeline should lead to fractal dimension (D) as described in Table 1. D is lower within p/p_0 range of 0.005–0.04, medium within 0.04–0.10, and higher within 0.10–0.20. Furthermore, fractal dimension of HNS revealed lower than that of TATB which accorded with the truth that TATB conglomeration sample owned abundant micropores and higher surface area.

3.3 Discussion

Superfine explosives were well-known for decades due to its expectant improvement for sensitivity and initiating performances. Early researches of superfine explosive focused on the reduction of particle size which worked intuitively on performance modification. Subsequent experience showed that superfine particles with similar particle size distribution would not always lead to expectative performance and the disturbance should result considerably from conglomeration. Surface area which summarized the particle size distribution and some of the conglomeration was then brought forward. The experiments showed that surface area should be more relevant than particle size to sensitivity and initiating performances of superfine explosives so that surface area turned to be major quality parameter in manufacture[15-16]. Unfortunately, surface area could not explain everything and there were some other parameters which regulated the sensitivity and initiating performance.

Table 1 Fractal dimension data calculated from desorption data

p/p_0	HNS	TATB
0.005–0.04	D=1.756 ±0.0232 r=0.99948±0.00651 N=5	D=2.29382±0.01739 r=0.99909±0.00527 N=5
0.04–0.1	D=2.197±0.02243 r=0.99806±0.00792 N=7	D=2.49799±0.00715 r=0.99949±0.00216 N=7
0.1–0.2	D=2.414±0.00491 r=0.99968±0.00172 N=11	D=2.55328±0.00096 r=0.99998±0.00031 N=10

Note: D mean the fractal dimension, r mean the correlation coefficients of the fitting line, and N mean the point number of the fitting line.

According to classical hotspot theory[18], initiation of non-homogeneous explosives consisted of initiation of hotspots and growth of explosion, initiation of hotspots should be more difficult while growth of explosion should be easier for superfine explosives than for ordinary explosives. When the superfine explosives were attempted in flyer impact experiments, shockwave pressure was far higher than necessary for initiation of hotspots and growth of explosion dominated within the initiation process. Therefore, flyer impact experiments[19-21] showed lower initiating voltage and lower initiating energy threshold for superfine explosives than ordinary explosives.

How to describe microstructure of superfine explosives? The parameters in existence such as particle size distribution and surface area should be expected to relate to the novel parameters supplemented in the text including BJH data, HK data, and fractal dimension. These should be expected beneficial to comprehension of microstructure-initiating performance relationship of the explosives though their relationship was not discussed sufficiently.

Microcosmic structure should play an important role from creation of hotspots to eyeable explosion. The microstructure parameters should be relevant to both the hotspots distribution and the growth of explosion. The sequent researches would be expected to detailed the relationship of microstructure and macroscopical initiating performance. There might be new-fashioned parameter which acted better in quality control and initiating performance.

4 Conclusions

Microstructure of superfine explosives conglomeration were detailed. HNS conglomeration consisted of cashew-like nanometer crystals which piled up tightly here or loose somewhere else to form the conglomeration sample and the surface area was measured up to 11.8 m^2 · g^{-1}. TATB conglomeration consisted of nanometer crystals which connected mutually to form framework-like conglomeration and the surface area was measured up to 24.77 $m^2 \cdot g^{-1}$. Both samples showed IV type desorption isotherms with their hysteresis loop ranged within really high pressure. BJH and HK curves showed higher pore volume and higher surface area before 12 Å and after 80 Å for TATB conglomeration than for HNS, while it was reverse within range of 12–80 Å. It seemed that micropores contributed to pore volume more than mesopores.

Desorption isotherm of both conglomeration samples were analyzed to show fractal characteristics. The fractal dimension behaved lower within the range of p/p_0 0.005–0.04, medium within 0.04–0.10, and higher within 0.1–0.2. Comparatively, TATB sample owned higher fractal dimension than HNS sample.

The microstructures of superfine explosives conglomeration should be researched more and new-fashioned parameter might be expected to act better in quality control and initiating performance.

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TATB 和 HNS 超细炸药的微结构和分形特性

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摘　要：采用溶剂-非溶剂重结晶方法制备了 TATB 超细炸药和六硝基芪（HNS）超细炸药，对其微结构行了扫描电镜测试、比表面积测试、氮气吸附法分析和分形分析。结果表明，HNS 超细炸药是由腰果状纳米颗粒以或紧密或疏松方式堆积而成的团聚体，比表面积为 11.8 $m^2 \cdot g^{-1}$。TATB 超细炸药是由纳米颗粒互相连接而成的团聚体，比表面积 24.77 $m^2 \cdot g^{-1}$。氮气吸附结果显示，HNS 和 TATB 两个样品均呈现 IV 型吸附曲线，滞后环均位于相对压力较高的区域。Barrett-Joyner-Halenda（BJH）和 Horvaih-Kawazoe（HK）曲线显示，在孔径 12Å 以下和 80Å 以上区域中，TATB 样品的孔体积和表面积大于 HNS 样品，在孔径 12 ~80Å 区域则相反，由此可见 TATB 的高孔体积和高表面积源于微孔区的作用，而非介孔区的作用。两个样品的吸附曲线均展现出分形微结构，分维数在 p/p_0 处于 0.005 ~0.04 区间较低，在 p/p_0 处于 0.04 ~0.10 区间中等，在 p/p_0 处于 0.1 ~0.2 区间则较高，这三个区间里，TATB 样品的分维数均都高于 HNS 样品。与样品表面积数据相比，BJH、HK 数据和分形分析提供的微结构信息更为详细，这将有助于对超细炸药团聚体微结构和微结构-性能关系的理解。

关键词：超细炸药；六硝基芪（HNS）；TATB；微结构；团聚体；吸附等温线；分形分析
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