Research paper

Microstructures of submicron TATB and their effects on TATB thermal properties

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Abstract

In order to study the microstructures of submicron TATB and their effects on TATB thermal properties, three different ultrafine TATB particles were prepared by supersonic airflow impacting method, recrystalling method and recrystalling–supersonic speed airflow impacting method respectively. Their particles size, particle shape and surface microstructure, thermal decomposition temperature and thermal performance were also discussed. The results show that D_{50} of all three samples was around 200 nm, most particles obtained by supersonic airflow impacting method were spheroidal or ellipsoid, particles surface was much smooth and particles size was asymmetry. While particles obtained by recrystalling method looked like strips with many defects on their surface, and particles obtained by recrystalling–supersonic speed airflow impacting method looked also like strips but with smooth surface and less defects. DTA exothermic peak and 5 seconds (5 S) deflagration point temperature of samples obtained by supersonic airflow impacting method and recrystalling –supersonicd airflow impacting method are close, yet DTA exothermic peak and 5 S deflagration point temperature of recrystalling samples falls more than 10 degree and activation energy falls about 8 $kJ.mol^{-1}$ compared with other two samples. It was reckoned that the particles defects of submicron TATB should have a remarkable effect on their thermal properties while particles shape and purity had a little effect on thermal properties.

Keywords : Microstructure, Thermal properties, Submicron, TATB

Introduction

When energetic materials are fined, their many physical and chemical properties are changed due to reduction of particles size and increase of specific surface area (SSA), and there also show some new special properties such as the critical diameter reducing, charge intensity increasing, mechanical sensitivity decreasing and shock wave transmitting more quickly and stably[1-2]. When TATB (1,3,5–triamido–2,4,6– trinitrobenzene) is fined, it maybe also possess these new properties, which is hopeful to improve its properties and extend its application fields[3].

Many methods can be used to prepare ultrafine TATB particles, such as airflow impacting method, recrystalling method, mechanical milling method and sonochemical synthesis method[4-6]. The preparation approach and technical conditions certainly affect TATB particles' microstructure (such as particle size, particle morphology, surface microstructure and crystal defects)[4], sequentially affect the ultrafine TATB properties and finally correlative products properties and application. In this study, three different submicron TATB samples are prepared by supersound airflow impacting method, recrystalling method and recrystalling–supersound airflow impacting method respectively, their microstructure and the effect of microstructure on thermal properties are also studied.

1. Experimental

1.1 Samples preparation

Three different microstructure ultrafine TATB samples were prepared by supersonic airflow impacting method, recrystalling method and recrystalling–supersonic airflow impacting method respectively according to ref.4–6.

1.2 Characterization of samples microstructure and properties

The particles size of TATB were measured with LS230 Coulter laser size analyzer, SSA was measured with BET surface area measurement, particles morphology and sur-

Table 1 The particles size data of three ultrafine TATBs

No.	Preparation method	Volume size/nm		SSA	Purity
		Average size	D50	$/m^2.g^{-1}$	/%
FTATB−1	Supersound airflow impacting	572	206	7.68	99.0
FTATB−2	Solvent/non−solvent recrystalling	476	184	9.06	93.0
FTATB−3	Recrystalling−supersound airflow impacting	473	194	10.03	92.4

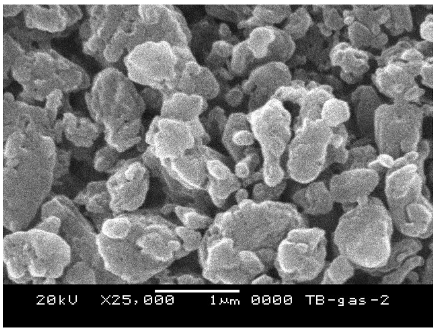

Fig. 1 The SEM of FTATB−1

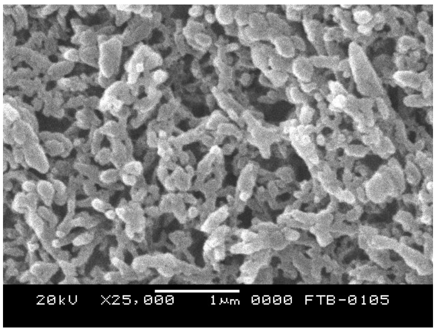

Fig. 2 The SEM of FTATB−2

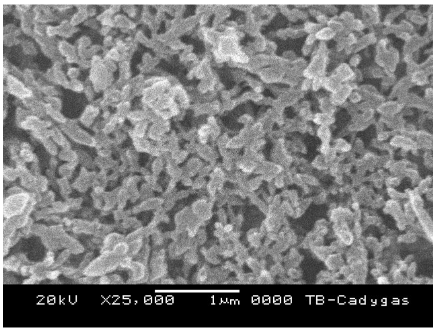

Fig. 3 The SEM of FTATB−3

face microstructure were characterized with scanning electric microscopy (SEM), samples purity was analyzed by high performance liquid chromatogram (HPLC).

The thermal sensitivity is an important parameter of explosives. Usually, we use 5 S deflagration point temperature to compare the thermal sensitivity of different explosives. According to ref.[7], 5 S deflagration point temperature was determined by encapsulated 30 mg mass in detonator shell firstly and above 30 such samples were prepared, then these samples were heated at different temperature which was above or under the pre−tested deflagration temperature respectively, and the deflagration time under each temperature can be obtained, so the 5 S deflagration temperature and activation energy can be calculated according to the following formula[7] :

$$\ln t = \frac{E}{RT} + \ln C$$

Where, t−the explosion deflagration time, S ;

E−the activation energy,J mol^{-1} ;

R=8.314 J $(mol\ K)^{-1}$;

C−constant.

DTA thermal decomposition temperature was measured according to ref.[8]. The DTA curve was measured by heated sample from room temperature to 500 °C with a heat rating of 10 °C min^{-1}. From the DTA curve, we can gain the information about melting peak and decomposition peak integrated energy and onset temperature.

2. Results and discusses

2.1 Samples size and purity

The volume average size data of ultrafine TATB samples prepared by three methods are shown in Table 1.

As shown in Table 1, particles size of supersound airflow impacting sample is 572 nm, bigger than the others whose average sizes are around 470 nm. While D_{50} of three samples is around 200 nm, all three samples are submicron ultrafine powders. As a whole, both the volume average size and D_{50} of three states ultrafine TATB powders are rather adjacent.

For SSA, supersound airflow impacting sample is much lower than the other samples which prepared via recrystalling process. When recrystalling sample is impacted by supersound airflow, the product, i.e. recrystalling−supersound airflow impacting sample, has a higher SSA than recrystalling sample.

From Table 1, it can be found that the supersound airflow impacting sample has the highest purity of 99 %, while the samples fined via recrystalling process has a lower purity of about 93 %, and 7 % is impurities which come from the recrystaling process. According to the preparation process, the impurities are water and sulfate acid which exist among or inside ultrafine TATB particles, this inclusive impurities can't be removed completely through washing and drying.

2.2 The particles shape and surface microstructure

The particles shape and surface microstructure of three TATB samples are shown in Figs. 1~3.

As shown in SEM pictures, most particles shape of supersonic airflow impacting sample is elliptic or spheroidal and the particles surface is comparatively smooth, but the particles size range is wide, some particles are much bigger while other particles are rather small, the particles size is asymmetrical. The samples particles shape and size prepared via recrystalling are similar, most particles of both samples show an anomalous strips shape, but recrystalling sample FTATB−2 particles surface has more defects than recrystalling−supersound airflow impacting samples FATTB−3, while the particle surface of FATTB −3 are more smoother than FTATB−2 particles, these observations are accordant to their preparation process.

2.3 Thermal properties

The DTA exothermic peak temperature and 5S deflagration point temperature are shown in Table 2.

As shown in Table 2, the thermal properties of ultrafine

Table 2 The thermal properties data of three submicron TATB samples

Samples number	DTA exothermic peak/℃		5 S deflagration point	
	Peak value	Extrapolate value	Temperature/℃	Activation energy/kJ mol^{-1}
FTATB−1	388.6	397.8	414.8	99.9
FTATB−2	367.3	376.2	401.6	91.8
FTATB−3	384.5	394.3	413.5	99.2

TATB are associated with the particles microstructure. Supersound airflow impacting sample FTATB−1 and recrystalling−supersound airflow impacting sample FTATB −3 have similar DTA exothermic peak temperature, 5 S deflagration point temperature and activation energy, but the three values of FTATB−1 and FTATB−3 are much higher than recrystalling sample FATTB−2. Concretely, compared with airflow impacting samples FTATB−1 and FTATB−3, both exothermic peak value temperature and extrapolate temperature of FTATB−2 are lower above 17 °C, 5 S deflagration point temperature falls above 10 °C and active energy reduces around 8 kJ mol^{-1}.

From above results, it is obvious that although three samples are submicron TATB powders with similar particles size, their thermal properties are different due to their different microstructures, i.e., the microstructure of submicron TATB has a remarkable influence on thermal properties. For FTATB−1 and FTATB−3, both have similar particle size, purity and anomalous particles shape, but FTATB−2 particles has more surface defects, these defects can form many hot spots under environmental thermal acting, this is helpful to promote the process of chemical reaction and thermal deflagration, therefore the FTATB−2 has lower thermal decomposition temperature, 5S deflagration temperature and activation energy. For FTATB−1 and FTATB−3, they have different particles shape and purity, but they have similar smooth particles surface and surface defects, they have similar thermal properties. Compared with FTATB−2, the airflow impacting samples FTATB−1 and FTATB−3 have smoother particles surface and less defects, the number of hot spots formed under environmental thermal acting is much less than recrystalling sample, so the airflow impacting samples have higher thermal decomposition temperature, 5 S deflagration temperature and activation energy. These results show that particles defects is the remarkable factor affecting the submicron TATB thermal properties, particles shape and purity have a relatively lower influence on submicron TATB thermal properties.

3. Conclusions

On the basic of above study results, following conclusion could be obtained :

(1) All supersonic airflow impacting method, solvent/ non−solvent recrystalling method and recrystalling−supersound airflow impacting method can prepare submicron TATB powders with average size of within 600 nm and D_{50} of around 200 nm.

(2) Most particles shape of supersonic airflow impacting sample FATTB−1 is elliptic or spherical, the particles surface is comparatively smooth, particles size is asymmetry and the purity is high. While most particles of recrystalling samples FTATB−2 show anomalous strip shape, the particles surface is coarse and has many defects, the purity is low. Recrystalling−supersonic airflow impacting sample FTATB−3 particles also show anomalous strip shape and purity is low, the particles surface is smooth.

(3) The DTA exothermic peak temperature, 5 S deflagration point temperature and activation energy of supersonic airflow impacting sample are close to that of recrystalling−supersonic airflow impacting sample, while the exothermic peak temperature and 5 S deflagration point temperature of recrystalling sample are much lower than other samples, its exothermic peak value temperature and 5 S deflagration point temperature are lower above 17 °C and 10 °C respectively than airflow impacting samples.

(4) The particles defects has a remarkable effect on the submicron TATB thermal properties, particles shape and purity have a relative lower effect on submicron TATB thermal properties.

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