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Investigation on Irreversible Expansion of 1,3,5-Triamino-2,4,6-trinitrobenzene Cylinder

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Abstract: In this study, the irreversible expansion of TATB cylinder is investigated. No evident variation of the lattice parameters is observed on TATB crystal. The density of TATB powder decreases by only about 0.02% after it suffered from thermal cycling process at the range from -54 °C to 74 °C, while the density of TATB cylinder decreases by about 1.0%. It is suggested that the density variation of TATB powder has little contribution to the density decrease of TATB cylinder. Therefore, the increasing interstices between TATB powder originated from the thermal cycling should be responsible to the irreversible expansion of TATB cylinder.

Keywords: TATB, irreversible expansion, XRD, lattice parameters

Introduction

1,3,5-triamino-2, 4, 6-trinitrobenzene (TATB) is the unique explosive fulfilled with American IHE standard up to now. It possesses excellent safety and good comprehensive properties. Thus, it is widely used as one of the main explosive formulations, such as PBX-9502 and LX-17. However, the TATB-based PBX explosives always show irreversible expansion under thermal cycling process [1-7], which may reach up to 1% of volume expansion from -54 °C to 74 °C and about 3% from room temperature to 280 °C. The irreversible expansion degrades their mechanical and explosive properties, and increases the shock sensitivity, which further produces some side effects on their application and storage.

Much effort has been made by researchers to investigate and control the irreversible expansion of TATB-based PBXs. For example, Zhang and co-workers theoretically studied the irreversible expansion of TATB crystals by means of DFT method [8]. They thought that TATB crystals were usually in the state of high potential energy at room temperature. When volume expanded during heating, TATB crystals arrived at a thermodynamically stable state, so the irreversible expansion happened. The opinion sounds reasonable, but they couldn't elucidate persistent irreversible expansion of TATB cylinder during repeated thermal cycling process [4-7]. Gee and co-workers utilized molecule dynamics and mesoscopic simulation to explain the irreversible expansion of TATB-based PBXs [9-14]. They thought that the crystal structure of TATB does not change under the thermal cycling, but its remarkable anisotropic expansion leads to crystal fragmentation, which resulted in the irreversible expansions of TATB crystallites and cylinder. They believed that all the crystalline anisotropy, particle size distribution and binder strength have effect on irreversible expansion. However, most of their simulations except the effect of binder strength [15, 16] had not been confirmed by any experiment up to now. It should be noticed that all these simulations aimed at the single crystal TATB, but TATB in practice are multicrystal with more defects and porosities contained. And what's more, these simulations were not related to the preferred orientation, which usually take place in the moulding process of the TATB based PBX [17]. So these results couldn't felicitously reflect the irreversible expansion of TATB powders and cylinders.

Willey and co-workers [16, 18] found that the quantity and size of the cavities of multicrystal TATB based PBX cylinder increased after it undergoing thermal cycling. They thought that additional voids account for the irreversible volume expansion, but they didn't point out clearly where the additional voids come from (between powders or in powders). As we know, the binder has an effect on the irreversible volume expansion, so it's hard to elucidate the source and mechanism on the ratchet growth of TATB-based explosive.

Kolb *et al.* employed X-ray diffraction techniques to investigate lattice parameters of single crystal TATB under thermal cycling [1]. They found that irreversible expansion of the single crystal TATB was not observed, but the cavities in multi-crystal powder, which probably leads to irreversible expansion, hasn't been taken into account. From the turning point of the thermal expansion of TATB crystal, Kolb draw a conclusion that a second order mechanical relaxation existed in TATB crystals. Hoffman and Humphrey *et al.* proposed that the second order mechanical relaxation at 34 °C probably leads to the irreversible expansion of TATB cylinder [19, 20], but the turning point of the thermal expansion disappeared by accurate thermal expansion measurement [21].

Therefore, this work is carried out to discuss which part of volume expansion accounts for the irreversible expansion of TATB cylinder under thermal cycling. The lattice parameter of TATB crystal is studied by X-ray diffractometer and Rietveld refinement, which is to investigate if there exist lattice parameter variation during thermal cycling process. The density variations of TATB powders and TATB cylinders are measured by density gradient tube and water displacement method, respectively, from which we can found out the origin of irreversible expansion, intraspace in powders. The size of TATB cylinders is measured by micrometers, which can tell us the effect of consolidate technology on irreversible expansion of TATB cylinders.

Experimental

Sample preparation

TATB was synthesized by Institute of Chemical Materials, China Academy of Engineering Physics. The mean diameter of the particles was about 15.7 μm with the purity over 99%. Under different pressure, TATB cylinder without binder was obtained by uniaxial pressing in a steel die at room temperature. The relative density of TATB cylinder was 91~98% of theoretical density.

Crystal structure and density measurement

X-ray diffraction patterns were collected on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation without any monochromator. Measurements were performed on TATB powders and cylinder before and after ten times thermal cycling from -54 °C to 74 °C. The thermal treating program is shown in Figure 1. The X-ray tube with vantec-1 detector was operated under the condition of 40 kV and 40 mA.

In-situ XRD detection was performed at 30 °C and 240 °C. A temperature chamber (TTK450) was used to precisely control the temperature during experiment. The details process steps were as follows: the first scan was done when sample was at 30 °C, the second scan was done after heating to 240 °C and maintaining for 2 h, the sample was subsequently cooled to 30 °C for the third scan. The above cycling scanning was performed more twice.

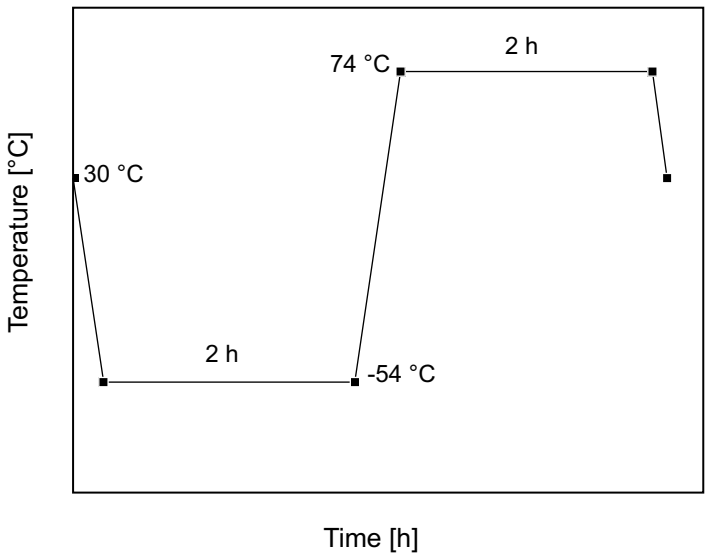


Figure 1. The curve of temperature versus time during thermal cycling process.

The diffraction patterns were evaluated by Rietveld analysis using the TOPAS software. The fundamental parameters approach (FPA) profile function was adopted to fit the experiment data using a Chebychev polynomial of fourth order and the 1=X/Bkg function. Tube tails information was used instead of receiving slit (RS) and fixed divergence slit (FDS) attributed to the use of Vantec-1 detector. The absorption correction was set to refine in order to correct the significant profile shape distortion caused by the low mass absorption of the sample. In addition, it was also necessary to refine zero error. The X-ray diffractometer was not equipped with a monochromator, so the Lorentz polarization (LP) factor for unpolarized radiation was zero. Crystal structure data for Rietveld refinement were as follows: space group P1, with Z=2, a=9.010 Å, b=9.028 Å, c=6.812 Å, and α=108.59 °, β=91.82 °, γ=119.97 °, and the density was 1.938 g·cm^{-3}.

Density and dimension measurement

The density of TATB powders and cylinder were determined at 20 °C using density gradient tube and water displacement method, respectively. The uncertainty was about 5×10^{-4} g·cm^{-3}.

The dimension of TATB cylinder was measured at 20 °C by micrometer, with a veracity of 0.001 mm.

Results and Discussion

As shown in Figure 2, the volume of TATB cylinder is composed of bulk crystal, cavity in TATB powders and interstice between TATB powders, whose variations can be used to explain the origin of irreversible expansion of TATB cylinder. The volume variation of bulk crystal can be obtained by comparing its lattice parameters before and after thermal cycling. The total volume change, the cavity variation in TATB powders and the interstices evolution between TATB powders can be obtained by comparing its density variation before and after thermal process.

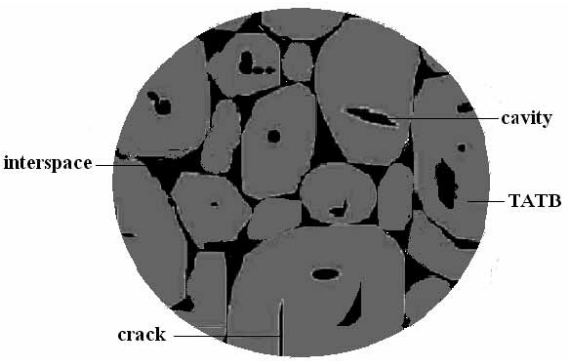
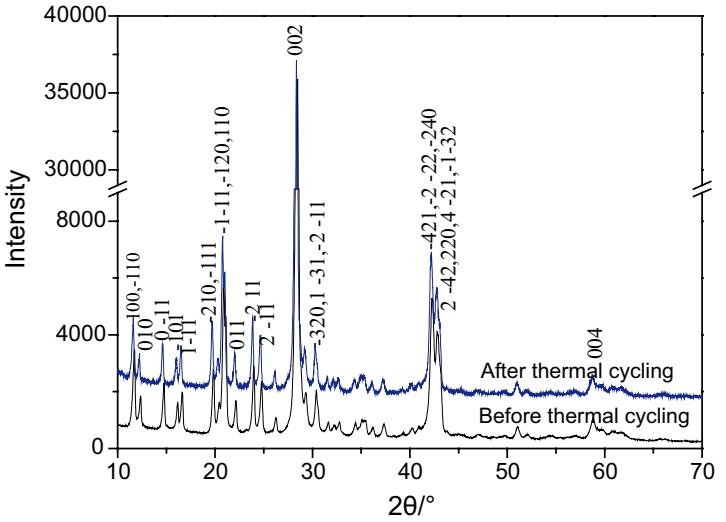


Figure 2. Schematic of volume composition of TATB cylinder.

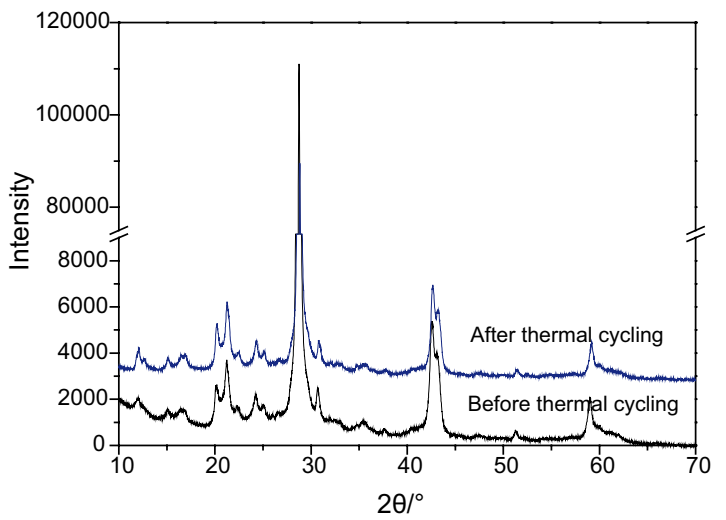
Lattice parameter of TATB

XRD analysis was performed to clarify effect of thermal cycling process on lattice parameters of TATB powders and TATB cylinder, and the results were shown in Figure 3. Figure 3A indicates that XRD pattern of TATB powder has the same peak position and shape after it suffering from thermal process, which implies that no crystal transformation happens. So it is impossible that irreversible expansion generates from formation of low density TATB crystal type. Compared with Figure 3A, it is obvious that the diffraction peak become broader when the powders were pressed to cylinders (Figure 3B), but their positions kept constant, which may indicate that the crystal fragmentation happened and more residual strain was obtained during the consolidate process. Through Rietveld refinement, lattice parameters of TATB powder before and after thermal cycling were obtained, as shown in Table 1. Errors of lattice parameters (a, b, c) are less than the values obtained from references [1]. The results show that no variation occurring to TATB lattice parameters undergoing thermal cycling from -54 °C to

74 °C. It is difficult to obtain accurate lattice parameter of pressed TATB crystal because of the broadened diffraction peak of cylinders.



A



B

Figure 3. XRD pattern of TATB before and after thermal process (0.02 °, 0.2 s/step), A) TATB powder, B) TATB cylinder.

Table 1. Lattice parameters of TATB powder before and after thermal process

TATB	a/Å	b/Å	c/Å	α/°	β/°	γ/°	Cell Vol/Å^3	R_{wp}/%
Before heating	9.014	9.030	6.820	108.69	91.78	119.96	443.02	8.36
After heating	9.012	9.030	6.818	108.66	91.78	119.97	442.89	10.46

Note: R_{wp} is a parameter used to evaluate the refinement results, which can be considered to be reliable when the value of R_{wp} is smaller than 15%.

In order to enlarge the possible irreversible expansion of lattice parameters of TATB powders, *in-situ* XRD and Rietveld refinement was performed to obtain the lattice parameters of TATB before and after heating to 240 °C. Figure 4 shows *in-situ* XRD spectra of TATB powders. It can be concluded that TATB at 30 °C and 240 °C has the same crystal type. The peak position 2θ of [002] decreases by about 1 ° when the temperature increases from 30 °C to 240 °C, which may result from the thermal expansion of interplanar distance of [002] crystal plane.

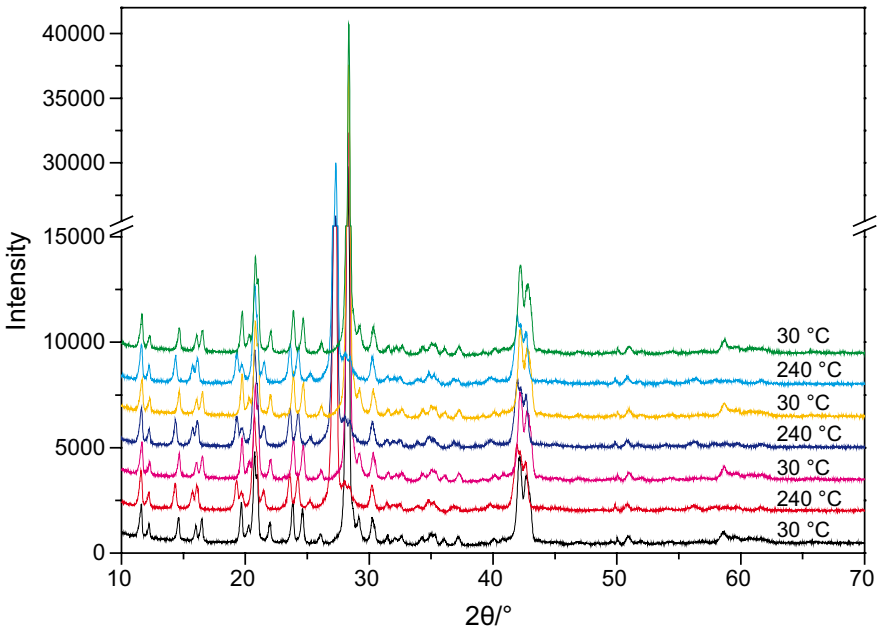


Figure 4. XRD pattern of TATB under 30 °C and 240 °C (0.05 °, 0.1 s/step).

The lattice parameters of TATB undergoing 30 °C to 240 °C thermal cycling are listed in Table 2. It is found that when the temperature rises, a, b, c- axis expand, while α, β angles decrease, and γ angle keeps constant, and these

changing can revert to the initial state when temperature fall down. It is also shown that no irreversible expansion occurs to TATB crystal undergoing three thermal cycling. The results measured use TATB powders are consistent with the single crystal measurements [1].

Table 2. Lattice parameters of TATB at 30 °C and 240 °C

T/°C	a/Å	b/Å	c/Å	α/°	β/°	γ/°	Cell Vol/Å^3	R_{wp}/%
30	9.016	9.033	6.827	108.68	91.77	119.97	443.70	10.76
240	9.036	9.049	7.067	108.53	91.50	119.97	462.43	10.22
30	9.015	9.032	6.827	108.68	91.76	119.97	443.67	10.01
240	9.035	9.050	7.069	108.53	91.50	119.99	462.48	9.74
30	9.016	9.031	6.827	108.68	91.76	119.97	443.64	9.97
240	9.035	9.051	7.068	108.54	91.50	119.98	462.45	9.71
30	9.016	9.033	6.827	108.68	91.76	119.97	443.77	10.07

Density and size distribution of TATB powders

Density of TATB powders was determined using density gradient method. The density of TATB powders before and after thermal process are 1.9179 g·cm^{-3} and 1.9175 g·cm^{-3}, respectively. It also shows that the density of TATB powders decreases by only 0.0004 g·cm^{-3}after the thermal process, the subtle difference may be result from test method. Someone may doubt that the particles would fracture and expose internal defects to the surface of new smaller particles. So the column fluid was able to wet the defect, and the TATB powder suffering from thermal cycling may show a slightly higher apparent density, which may counteract the density decrease caused by irreversible expansion. However, the size distribution of TATB powder shows no obvious difference before and after thermal cycling, which demonstrates that the particle fracture didn't take place.

The volume of TATB powders, composed of bulk crystals and cavities, does not change after thermal process. Therefore, it is demonstrated that no irreversible expansion happens to TATB powders. It can be concluded that the irreversible expansion of TATB cylinder does not originate from TATB powders.

Dimension and density of TATB cylinder

The density of TATB cylinder is 1.768 g·cm^{-3} ~1.899 g·cm^{-3}. Tables 3 and 4 show the density and size of TATB cylinder before and after ten-cycle thermal cycling process. Table 3 shows that the density of TATB cylinder has a remarkable decrease (about 1%). There is strong influence of the ratio of diameter to length on the density change of TATB cylinder. For example, TATB cylinder with Φ20 mm×3 mm shows a higher decrease in density than the cylinder with

Φ10 mm×10 mm and Φ20 mm×20 mm.

Table 3. The density of TATB cylinder before and after thermal process

Size	Sample I.D.	Initial density [g·cm^{-3}]	Final density [g·cm^{-3}]	density change%
Φ10mm×10mm	1	1.811	1.797	-0.75
Φ10mm×10mm	2	1.768	1.786	-1.0
Φ10mm×10mm	3	1.898	1.878	-1.05
Φ10mm×10mm	4	1.899	1.879	-1.07
Φ20mm×20mm	5	1.815	1.795	-1.08
Φ20mm×20mm	6	1.846	1.830	-0.88
Φ20mm×20mm	7	1.879	1.862	-0.90
Φ20mm×20mm	8	1.881	1.864	-0.89
Φ20mm×3mm	9	1.886	1.861	-1.30
Φ20mm×3mm	10	1.864	1.833	-1.66
Φ20mm×3mm	11	1.881	1.860	-1.12
Φ20mm×3mm	12	1.882	1.861	-1.11

Table 4. The dimension of TATB cylinder (Φ20 mm×20 mm) before and after thermal process

Sample I.D		5	6	7	8
Axial direction	Initial length, mm	20.42	20.373	20.326	20.317
	Final length, mm	20.545	20.495	20.457	20.431
	Length change, %	0.61	0.6	0.64	0.56
Radial direction	Initial diameter, mm	20.112	20.073	20.079	20.109
	Final diameter, mm	20.165	20.13	20.131	20.158
	Diameter change, %	0.26	0.28	0.26	0.24

Notes: a, The values were an average dimension of three measurements in different position.
b, The dimension expansion of other cylinder was not measured because the dimension was very small and the relative error would be much bigger.

Table 4 indicates that the irreversible expansion percentage of Φ20 mm × 20 mm TATB cylinder is 0.26% ±0.02% at radial direction and 0.60% ±0.04% along the axis direction. There is more irreversible expansion along axis than that of radial direction, which can be attributed to that more pressure was executed on TATB cylinder along the axis direction and preferred orientation of [001] crystal plane occurred perpendicular to the axis direction. Because of the distinct anisotropic expansion of TATB crystals, TATB cylinders would have more expansion along the axis direction. In this condition, the newly developed interstices would be

more and bigger along the axis direction, and an extra irreversible expansion would take place. However, these possibilities haven't been considered anywhere. So the isotropic expansion and preferred orientation would play an important role in the irreversible expansion of TATB cylinders.

Combined with the results above, we can conclude that the newly developed interstices between TATB powders, induced by thermal process, such as cracks, loosening, cavities, fully account for irreversible expansion.

Conclusions

The really source of irreversible expansion is of great importance for understanding its mechanism. This work has demonstrated that TATB crystallite and TATB powders have little contribution to irreversible expansion of TATB cylinder. The enlarged and newly developed interstice between TATB powders during thermal cycling process should be responsible for its irreversible expansion. It is clear that the isotropic expansion and preferred orientation would play an important role in the irreversible expansion of TATB cylinders. Therefore, our results could provide academic guide for inhibiting irreversible expansion of TATB-based explosives through optimizing thermal treating method.

Acknowledgement

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