MORPHOLOGY CONTROL OF NTO CRYSTALS WITH VARIOUS RECRYSTALLIZATION TECHNIQUES

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Abstract

Various recrystallization techniques has been applied to control morphology and size of NTO(3-nitro-1, 2, 4-triazole-5-one) crystals. With cooling method, it was found that the size of NTO at aqueous solution was controlled in the range of 5 to 500㎛. The spherical or cubic shapes of particles were obtained by adjusting operating conditions. Hexagonal and cubic shaped crystals of NTO were also obtained by sonication and evaporative method using aqueous solution of NTO. Their particle sizes were ranged 20 to 30 ㎛. In gas anti-solvent method with NTO/DMF and NTO/DMSO solutions, cubic type of NTO was obtained and the range of their sizes was 0.5-2㎛.

Introduction

NTO(3-nitro-1, 2, 4-triazole-5-one) is one of the promising explosives with less sensitivity. However, morphology of NTO particles as-synthesized is typically jagged rod-like shape that has a tendency to agglomerate. Subsequently, those particles make it difficult to predict the packing density and final performance as an explosive will be unstable. Horst et al.[1] have reported that growth habit of RDX(cyclotrimethylene trinitroamine) crystals is changed not only with solvents but also with level of supersaturation. Steen et al.[2] have shown that organic solvents can be used to improve the crystal quality(shape and the surface smoothness, etc.) of RDX base PBX which directly influences on the sensitivity of the explosive compound. Solventing out has been adopted for the particle size modification of TATB(1,3,5-triamino-2,4,6-trinitrobenzene) by Firsich et al.[3] in the sulfuric

acid or DMSO/NaOH solution. Those results imply that the impact sensitivity of explosives is primarily dependant on their molecular structures, but, desired performance could be accurately controlled by designing crystal shape and size distribution, etc. through recrystallization.

In this study, efforts have been directed to search proper solvents for NTO recrystallization with desirable morphology. Solubilities of NTO in dipolar aprotic and protic solvents have been measured by means of visual polythermal method. With those solvents, crystallization of NTO has been investigated by various recrystallization techniques using cooling method, sonication, evaporative method and gas anti-solvent method. The morphological change of the NTO crystals with these crystallization techniques is discussed.

Experimental Results and Discussion

Solubility of NTO

The solubility of NTO as shown in Fig. 1 was determined in six solvents over the temperature range of 10°C to 70°C using polythermal method. The six solvents was: DMF(dimethylformamide), DMSO(N,N-dimethyl sulfoxide), methanol, acetone, tetrahydrofuran and distilled water. The temperature of crystal observation cell with 20-30ml is controlled by heating media which was circulated by thermostat(Lauda, RM20S and PM351-1). The temperature of the cell was measured by RTD digital thermometer(Fluke, 2180A).

Recrystallization of NTO

Recrystallization of NTO by Cooling Method : The experiments were performed in batchwise operated crystallizer. The crystallizer was a draft-tube type with external baffles, a 300ml vessel with 60mm diameter and was equipped with an agitator, marine propeller type with 30mm diameter at a speed in the range of about 400 to 700 rpm. Thermostatic fluid was circulated from a thermostat, with accuracy of 0.05K through the outer jacket of crystallizer. The analysis of crystal size distribution, shape and mean crystal size was carried out by image analysis system(VIDIS, Karl Zeiss) with optical and electron microscopes.

For nucleation from solution cooled down at constant rate, Nyvlt proposed the relationship between the maximum allowable undercooling (i.e. metastable zone width), ΔT_{max} and cooling rate, b as followings:

$$\log b = \log (k/a) + n \log (\Delta T_m) \qquad (1)$$

where $k = k_n (dC_s/dT)^{n-1}$.

The maximum allowable undercooling ΔT_{max}, was taken as the difference between the equilibrium temperature and the temperature at

which nuclei were defected for each particular cooling rate. The equilibrium temperature was obtained from the experimentally determined solid-liquid diagram. Fig. 2 shows the plots of cooling rate against maximum undercooling in log-log coordinates for saturation temperature.

As shown in Fig. 2, the maximum allowable undercooling (i.e. maximum allowable supersaturation) varies with cooling rate and equilibrium temperature. The relationship among them can be expressed as the following relation.

$$\Delta T_m = c_1 b^l T_s^m \qquad (2)$$

The values of c_1, l and m obtained in this study are 144.6, 0.0905 and -0.47, respectively.

The mean crystal size is complex functions of nucleation and growth, which are functions of process variables such as agitation rate, feed composition and production rate. These functions are therefore related to the supersaturation. Supersaturation is closely related to metastable zone width in unseeded batch cooling crystallizer[4].

The crystal size increases with decreasing supersaturation. Some scattered data result from the difference of the operating conditions like solid contents, agitation speed, initial concentration. The average crystal size is in the range of 5 to 500 micron, which depends mainly on the supersaturation. In this cooling method, spherical and cubic shaped NTO crystals were obtained.

Recrystallization of NTO by Evaporative Method and by Sonication : Recrystallization of NTO in the aqueous solution of 1wt% was performed by evaporative technique. The pressure of the crystallizer was maintained about 230 torr in order to boil the solution at 70°C. When the temperature of the solution increases from 20 to 70°C, heating rate was varied at 0.25-2.5°C/min. As heating rate was increased 0.25 to 0.5°C, content of the crystals with hexagonal or tetragonal prism shapes increased. However, when heating rate was further increased, contents of hexagonal shapes are decreased and particle size distribution seems to be broaden. At heating rate of 1°C/min, crystal shapes were observed as solution temperature was increased from 50 to 70°C. As temperature of solution was increased up to 65°C, aspect ratio of hexagonal shaped crystals is found to be reduced.

Ultrasound energy with 20-50kHz has been applied during nucleation at 5wt% aqueous NTO solution. In this experiments, crystal morphology was found to change with temperature, sonication time and applied ultrasound power. Crystal shapes were mostly cubic and their sizes were ranged 20 to 30 ㎛. Fig. 3 shows typical NTO crystals obtained by sonication.

Recrystallization of NTO by Gas Anti-solvent Method : NTO is dissolved in a liquid solvent. The solution is contacted with SCF(CO_2) which can penetrate into and expand the liquid solvent but has low solvent power with respect to the solute, and then, the solute is precipitated due to the decreasing solvent power of the liquid solvent. DMF and DMSO were selected as organic solvents for the NTO on account of their good dissolving power toward the NTO and their high expansivity when contacted with carbon dioxide. 20wt% NTO/DMF, and NTO/ DMSO solutions were used. Carbon dioxide(99.9%) was prepared as anti-solvent and used in all the experiments.

For recrystallization experiments the pressure of 1470 psia was chosen to get enough expansivity of both DMF and DMSO at given temperature 25℃ with 20wt% of NTO/DMF and NTO/DMSO solutions. For both solutions similar results were obtained. SEM photomicrographs of original and GAS-processed NTO particles show that the resulting powders were cubic type of 0.5~2㎛, as shown in Fig. 4, compared to the needle shape of 20-50㎛.

Summary

For the NTO crystals recrystallized in this work, sensitivity tests have been performed by using a weight drop tester and friction sensitivity tester(Julius Peter, Germany). It was found that impact sensitivity of some products was much better than that of commercialized NTO(SNPE, France). Also friction sensitivity of our products was found to be comparable with that of NTO from SNPE. Those results indicate that final performance of explosives depends on morphology and size of explosive crystals which is controlled by recrystallization. Now, scale up process for some good results is being under construction.

References

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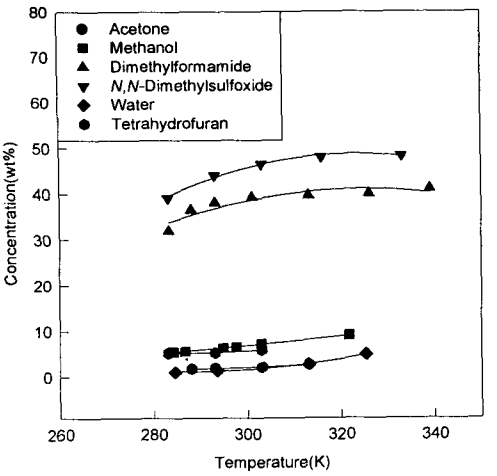

Fig. 1 Solubility of NTO

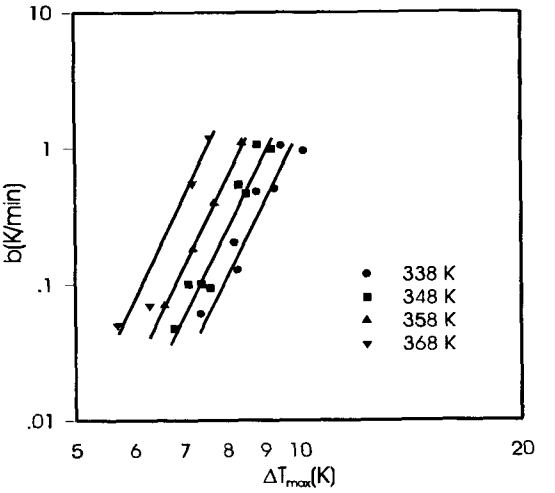

Fig. 2 Plot of b(cooling rate) versus $\triangle T_m$

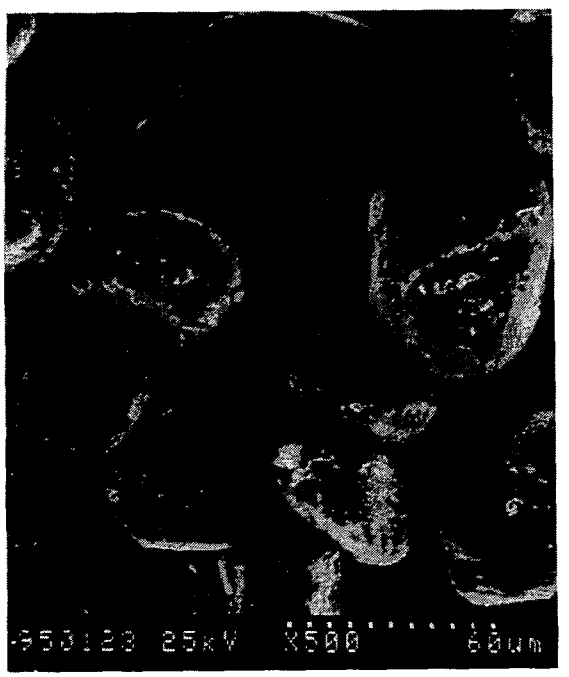

Fig. 3 NTO Crystals by Sonication

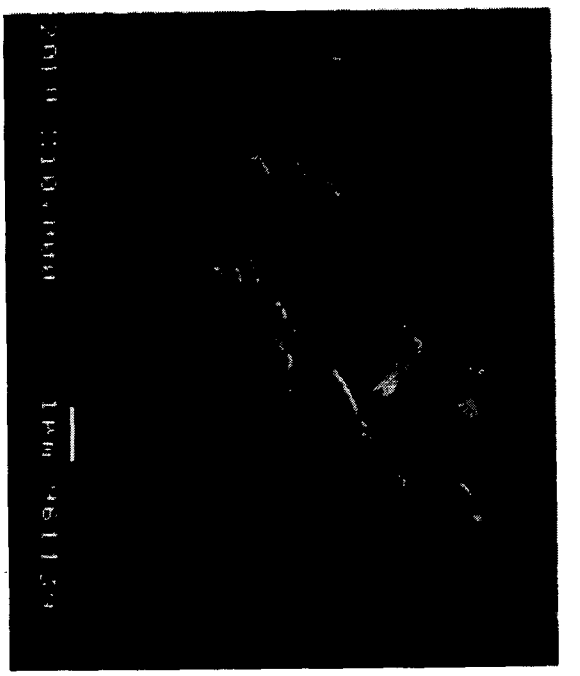

Fig. 4 NTO Crystals by Anti-Gas Solvent Method