



Observation of nanoscale hot-spot generation on a 2, 4, 6-trinitrophenol (TNP) single crystal

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ABSTRACT

An energetic material (EM) creates a local thermal point when it accepts energy and the EM will explode due to thermal decomposition when the hot-spot temperature reaches the explosive temperature. The initial stage of the hot-spot formation on 2, 4, 6-trinitrophenol (TNP) single crystal has been observed at the nanometer scale using atomic force microscopy (AFM). The hot-spot generation has been directly initiated by means of an AFM tip. The phenomenon is accompanied by producing agglomerated spherical-like nanoparticles due to a low-temperature decomposition of TNP. It has been observed that the agglomerated particles are produced outside of the stimulated region. The observed decomposition process at the nanoscale doesn't lead to a self-sustaining shock as detonation or explosion. The results are of interest in relation to explore the origin of deformation-induced chemical decomposition or detonation of EM.

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1. Introduction

Knowledge of the behaviour of EM subjected to phenomena at the nanometer scale is a main key to better understanding the nature of the initiation process of explosions. At present it is accepted that the violently decomposition process of EM involves the combined effect of heat transfer, chemical decomposition, and mechanical response [1,2]. Such coupled thermal–chemical–mechanical behaviour of material during decomposition is not easy to explore on a small scale by the usual methods because in many cases the accuracy of experiments have been limited due to the high speed of chemical reaction, the heat transfer and the destruction of the material under investigation [3]. The chemical–mechanical decomposition of EM is not fully understood; especially the preliminary mechanisms of the decomposition are not firmly established [4]. Nevertheless, due to strong experimental evidence the model of hot-spot formation is generally accepted [5–7] and the hot-spot model can be described as follows: during the mechanical excitation of an EM the mechanical energy is converted into a heat and it is left concentrated in a small region. The size of hot-spot must at least be comparable with molecular dimensions of EM, and thermal ignition then occurs if the hot-spot temperature reaches the temperature of decomposition. Thus, it is evident that the real origin of ignition should be explored at the nanometre scale, and atomic-force microscopy (AFM)

techniques provide one of the best possible solutions to study such behaviour.

Usually, the studies of explosive materials using an AFM have been focused on the investigation of the surface structure of EM. In particular, the investigation of surface evolution of pentaerythritol tetranitrate (PETN) organic films attributed to the bulk surface diffusion [8], the observation of molecular distortion in cyclotrimethylene trinitramine (RDX) molecular crystals due to shock or impact loading [9], the study of size and surface characteristics of trinitrotoluene (TNT) crystals [10], the fabrication of ultra thin layers of PETN and cyclotetramethylene tetranitramine (HMX) at the nanoscale [11], the conversion between δ -HMX and β -HMX phases due to the heating [12], and nanometer scale thermal destruction of PETN using a heated AFM tip [13] have been reported. However, an AFM opens a wide range of surface investigations at the nanometer scale, so here the involved AFM techniques are focused on nanomechanical initiated destructive effects. These are nanoindentation, nanolithography, friction etc. [14], and these techniques could be utilised to reveal new aspects of the hot-spot formation at the nanoscale.

Here, we report on the first direct initiation of the hot-spot formation on a surface of 2, 4, 6-trinitrophenol single crystals at the nanometer scale by an AFM tip. Immediate AFM imaging of the selected region revealed the destructive changes of TNP crystals, and allows a first estimate of evolution of the hot-spot phenomenon at its initial stage.

2. Experimental

The molecular formula of TNP is $C_6H_3N_3O_7$. According to the XDR experimental data [15] the TNP crystal has the orthorhombic crystal system (point group $mm2/C_{2v}$) and crystallises in a

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noncentrosymmetric space group (Pca2₁). The unit cell of TNP consist of 8 single molecules with $a = 9.25 \text{ \AA}$, $b = 19.13 \text{ \AA}$, $c = 9.7 \text{ \AA}$, $v = 1720 \text{ \AA}^3$ [16,17]. TNP crystals were obtained from an aqueous saturated solution ($\sim 5 \cdot 10^{-2} \text{ mol/l}$ at 22 °C) by depositing various 50–150 μl droplets on a substrate at room temperature. The substrate consists of silicon chips evaporated with gold resulting in a polycrystalline surface with an average roughness <5 nm. The chips, together with a flat dish filled with $\sim 100 \text{ ml}$ water, were covered by a large dish protecting the growing crystals from dust and air turbulences. Depending on the droplet size, dry, yellow TNP crystals were ready to use after 1–2 days.

Atomic force microscope (Nanotec Electronica SL, Madrid, Spain) was used to carry out the nanomodification and imaging of TNP micro-sized crystals. AFM tips (Mikromasch Co) with an improved wear resistant silicon nitride coating (Si₃N₄) compared to the native silicon oxide layer were used due to the following reason. A direct contact between TNP and Si could occur when a silicon oxide layer of a silicon tip becomes worn. In this case a chemical reaction, supported by a mechanical stress, between TNP and silicon oxide cannot be excluded. In such a case the chemical reaction may form silicon picrate. Metal picrates are known to be more sensitive to impact than just pure picric acid. A silicon nitride coating instead exhibits a higher chemical inertness to acids than silicon. The probe has a conical shape. The tip radius is 20 nm, the full tip cone angle is 30° as reported by the manufacturer. The calculation of oscillation parameters and force constant of cantilever were done using corresponding routines which are implemented in the AFM control software WSxM. The cantilever has a resonance frequency of 312 kHz, a Q factor of 602, and the force constant is 31.2 N/m. All AFM images have been captured using the intermittent contact mode also known as tapping-mode. All measurements and modifications of TNP crystals have been carried out under ambient conditions.

Indentation and ploughing techniques were used for destructive modification of the TNP crystal surface. The main aim of applying these AFM techniques was to initiate the destruction process of EM at the nanometre scale. Indentation is the best method for a single pit formation in which the external mechanical effect is limited by the contact area of a few square nanometres at a specified location on the surface. Ploughing involves a scratching of the surface by the tip with a large external force using the contact mode. Alternatively in intermittent contact mode the force interaction can be increased by adjusting the amplitude of oscillation (“hard tapping”).

3. Results and discussion

In Fig. 1 we show the illustration of the TNP molecules arrangements with respect to unit cell and crystallographic planes. Hydrogen atoms are not drawn. Molecular representations are performed with the Mercury 2.3 software (Cambridge Crystallographic Data Centre). The geometric representations of the crystal were made with KrystalShaper 1.1.6 (JCrystalSoft) software. So called slide planes or slip planes are present in the crystal as depicted by the grey rectangles. They represent the planes where the crystal is able to undergo a plastic deformation by a dislocation motion.

Images obtained with an atomic force microscope are always a convolution of the probe geometry and the shape of the features being imaged. If the probe is much smaller than the features of surface being measured, then the probe-generated artefacts will be minimal. If the curvature radius of tip is comparable with the size of features, then the probe generated artefacts will be significant. The recognition of the artefacts in AFM imaging is discussed elsewhere [18,19].

So, the exact determination of the shape of crystals using AFM topography data is an ambiguous task since the AFM tip may limit artefact free imaging of trenches and flanks. However, as shown in Fig. 2(c) the layered structure of the crystal is clearly visible in form of steps. This observation corresponds to results of the numerical

modelling of the crystal structure of TNP [17]. Even more it was observed that flat upper surface of TNP crystal has patterned substructure. A cross sectional height profile (not shown) shows the stepwise substructure. The average height of steps had been estimated by measuring the heights within the several height profiles collected at different positions on an upper surface of the TNP crystal. The average height of step is $0.94 \pm 0.15 \text{ nm}$. To conclude, tip shape and relative position between tip and sample are adequate for further analysis. Patterns on surfaces of EM were also observed on fractured [10] or shocked [20] cyclotrimethylenetrinitramine (RDX), where the phenomenon was called “river patterns”.

In Fig. 2(a) a shaded topography image of TNP is shown as grown on the gold substrate. TNP crystals often appear with small cracks and defects on the surface. Due to the fast growth conditions it is supposed that the structure is a set of cross-linked and coupled small crystals. This been previously demonstrated with the help of scanning electron microscopy [21,22]. Still some facets of small coupled crystals are visible on the left side of the bar-shaped TNP polycrystal (see Fig. 2(a)).

During the first scanning in the intermittent contact mode nothing unusual has been observed (see Fig. 2(a)). The second scan (not shown) has been done immediately afterwards, the time for each image acquisition is 290 s. It is important to emphasise that not by any means a surface modification within the selected region was performed. The second scan is characterised by the presence of several failure scan lines, which were located approximately at the centre of the selected region. In Fig. 2(b) the third scan is presented, which proceeded completely undisturbed. In this image the presence of a new object on top of the surface is obviously observable.

At first glance it is reasonable to assume that this object originates from the TNP crystal and that its generation was initiated to some extent by the tapping tip. It was inspected with care that the new objects are no wear particles lost by the tip. Namely the phenomenon was observed very often during the experiments and the tip was not abnormally worn, as can be seen by the unaltered quality of the images.

Assuming the dissipated energy per time from the tapping tip is sufficient to initiate the chemical decomposition of TNP molecules it still remains unclear, why this energy is insufficient to decompose the crystal at any other positions on the surface. But exactly this is the case. A second unsolved problem is the chemical composition of the new objects, which appear as nanoparticle agglomerates. Probably, the objects are the result of an initial step of decomposition of TNP molecules, which is not accompanied by the extensive production of heated gases CO₂ and NO₂ like during an explosion. Oxidation of TNP in aqueous media for instance leads to the release of nitro groups from the aromatic ring to form non-nitrogenated phenolic compounds [23]. Phenol, benzoquinone, maleic, and oxalic acid have been detected as soluble products during the electrolysis of TNP. Even the formation of a polymer from aminophenols was discussed [23]. The elimination of nitro groups leads to volatile molecules still aromatic or at least to molecules with π -electrons. Several complexes based on π - π interaction and hydrogen bonding or as an acidic ligand to form salts with polar aromatic or non-aromatic molecules through specific electrostatic interaction are known from the literature, namely 1:1- or 2:1-complexes with aromatic systems like orthonitroaniline [24], benzamide [25], 2-nitrophenol [26], anthranilic acid [27] and benzyldimethylamine [28]. To verify such an assumption in the present case of TNP crystals X-ray diffraction analysis or spectroscopy methods would be helpful, however the problem of collecting a sufficient amount of agglomerates is not solved yet. At least a partial chemical decomposition followed by a re-solidification of amorphous or crystalline phase is not excluded.

As it known, once the ignition of EM has been started on macroscale, a complete conversion into gaseous species appears. In contrast, the observed spontaneously occurred reaction or decomposition on nanoscale does not stimulate the same response of the surrounding

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