INVESTIGATION OF THE MICRO STRUCTURE OF ENERGETIC CRYSTALS BY MEANS OF X-RAY POWDER DIFFRACTION

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ABSTRACT

Mechanical sensitivity of energetic materials is discussed as a function of particle size and lattice defects. Therefore an approach is made to quantify and characterize lattice defects of the energetic powders RDX and HMX using X-ray diffraction. The mechanical properties of these cyclic nitramines are supposed to be dominated by different defect mechanisms – deformation twinning and dislocation slip. The energetic powders and the line shape standard SRM 660a (NIST) were measured on a Bragg-Brentano Diffractometer D5000 (Bruker-AXS), and the diffraction patterns were evaluated by Rietveld- and peak profile analysis using Williamson Hall plots. Additionally, preparing samples as thin powder layers was tested in order to reduce line broadening due to low absorption. The investigations reveal interesting details. Characteristic line broadening was found for RDX and HMX pointing to a comparably higher micro strain in HMX. Anisotropic line broadening was found for RDX and discussed in terms of strain fields of dislocations.

INTRODUCTION

Mechanical sensitivity, an important issue for energetic materials, has been discussed as a function of particle size and lattice defects. Therefore concepts were developed during the last decade in order to reduce defect concentrations applying careful crystallization and processing methods. Particularly, energetic nitramines as HMX and RDX are in the scope of interest, and for these materials reduced sensitive industrial products are already procurable [1, 2].

An approach is made to quantify and characterize lattice defects in energetic materials by means of X-ray diffraction evaluating the broadening of diffraction lines. The broadening, however, represents the geometry of the measuring system and sample features as size, strain, diffuse scattering, misfits between phases, etc. Crystal size and lattice distortion broadening are usual present concomitantly. The Warren Averbach-method [3] solves the problem of the separation of
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size and strain broadening revealing the root mean-squared strain ($\sqrt{\langle \varepsilon^2 \rangle}$). Williamson and Hall suggested that the full width at half-maximum (FWHM) of diffraction profiles can be written in terms of reciprocal units as the sum of strain and size broadening, with size broadening being independent and strain broadening depending on the diffraction order [4, 5]. A crucial point in this method is the physical model placed behind the root-mean-squared strains. In most cases strain is caused by dislocations, and displacements have a well defined spatial distribution and the root-mean-squared strain is far from being constant [5].

**CRYSTAL AND REAL STRUCTURES**

RDX ($C_3H_6N_6O_6$) crystallizes in the orthorhombic space group Pbca with the lattice parameters $a=13.182$, $b=11.574$ and $c=10.709$ Å [6], $Z=8$. Measured and calculated densities amount to 1,816 and 1,806, respectively. Armstrong and Elban described that the mechanical properties of RDX are explained by the difficulty of moving individual dislocations. An $[-100](040)$ edge dislocation was constructed by Armstrong et al. in order to explain the $(010)$ slip reported by Cinnick and May in 1969. Later on Elban, Armstrong and colleagues reported the occurrence of slip on $(021)$ and $(02-1)$ systems [7].

HMX ($C_4H_8N_8O_8$) crystallizes in four phases; $\alpha$-, $\beta$-, $\gamma$- and $\delta$-HMX. $\beta$-HMX is the room temperature stable phase with the highest density. Choi and Boutin found space group $P2_1/c$ with the lattice parameters $a=6.54$, $b=11.05$, $c=8.70$ Å and $\beta=124.3^\circ$, $Z=2$. Measured and calculated densities amount to 1.894 and 1.90 g/cm$^3$. [8] The internal properties of $\beta$-HMX seem to be dominated by crystal twinning. $(101)$-twins were observed in crystals growing from solutions and when crystals are exhibited to mechanical stress, and the deformation twinning was found to be reversible at low stress [7, 9].

**EXPERIMENTAL**

Diffraction patterns were measured of HMX and RDX with particle sizes of a few microns with a diffractometer D5000 from Bruker AXS, equipped with copper tube, vertical soller slits (2.3°), Ni-$k\beta$-filter, divergence and detector slits of 0.3° and 0.1 mm, and rotating sample holder. For determining the geometrical profiles of the systems the standard reference material SRM 660a was measured under the same conditions as the energetic materials. This line position and line shape standard is especially recommended for size-strain investigations as it is approximately strain-free and yields no size broadening. It consists of a fine Lanthanum Hexaboride powder with aggregates of crystallizes in the 2 to 5 µm range [10].

A preliminary series was measured with conventional sample preparation, filling powders up to the edge of a standard sample holder and flattening the surfaces with a glass plate. Patterns were
measured between 5 and 90°2θ with a step width of 0.01°2θ and a measuring time of 8 s/step. As absorption broadening was found with these measurements, particularly with the energetic materials, a second series was started, preparing samples as thin powder layers on a wafer or an aluminum plate, in order to reduce absorption broadening by reducing the diffracting sample volume. The patterns were measured in selected 2θ ranges; each sample was measured twice, freshly prepared, with step width of 0.005 2θ and 10 s measuring time per step.

EVALUATION

The diffraction patterns measured with common sample preparation were evaluated using the full pattern fitting tools of the program TOPAS from Bruker/AXS on the basis of so-called hkl-phases and the ray tracing fundamental parameter approach. Thus phases were identified, peaks were indexed, and peaks with minimal or without overlap were identified as »single peaks«.

The single peaks were fitted using the split-Pearson VII (SPVII) analytical function of program TOPAS yielding Full Widths at Half Maximum (FWHM) of the peaks, which were reduced by the geometric peak width obtained from the standard measurements, in order to obtain pure sample broadening. The data were evaluated in terms of reciprocal units as described by Williamson and Hall [4]. Therefore reciprocal peak widths \( \beta^* = \frac{2 \Delta \theta}{\lambda \cos \theta} \) and linear regression lines were fitted in the low d*-range. The slopes and intercepts of linear regression lines with the y-axis are discussed in terms of micro strain and inverse particle size. Additionally, deviations of the reciprocal peak widths from regression lines were determined and related to their peak indices, and systematic deviations were compared with anisotropic defect models reported in literature.

The linear absorption coefficients and penetration depths were calculated as described by Klug and Alexander (1974) for estimating peak broadening due to low absorption. Calculated penetration depths are 16 µm, 642 µm and 614 µm for LaB6, RDX and HMX, respectively.

FULL PATTERN FIT

Figure 1 shows for example a diffraction pattern of HMX and its full pattern fit. The peak positions and the indexing identify separated peaks of RDX at 13.07 (111), 13.40 (200), 16.51 (002), 17.35 (021), 17.83 (102), 20.35 (220), 21.99 (221), 25.35 (131), 30.42 (322), 31.14 (420), and of HMX at 14.70 (011), 18.28 (110), 20.53 (10-2), 22.06 (11-2), 23.02 (120), 27.19 (031), 29.64 (022), 31.90 (13-2), and 33.17 (200).
Figure 1. Diffraction pattern and “hkl-phase fit” of the HMX-sample; indexing and identification of separated peaks for single peak analysis.

**COMPARISON OF PREPARATION TECHNIQUES**

Figure 2 shows measured and fit peak profiles of RDX from conventional samples preparation and thin particle layers. With conventional sample preparation broad asymmetric peaks were measured due to the low absorption of the energetic materials. Preparing samples as thin particle layers reduced asymmetry and peak widths from 0.123 to 0.053°2θ FWHM for RDX(111)-peak. Thus, the preparation as a thin particle layer reduces the penetration depth and therefore the absorption broadening significantly. However, the high resolution obtained from powder layers are gained at the expanse of peak intensities.

Figure 2. Diffraction peaks of commonly prepared RDX (left) and a powder layer (right) fitted by SPVII.
Figures 3 and 4 show Williamson Hall plots of RDX and HMX obtained with thin particle layers. The reciprocal peak widths of RDX range between 0 and 0.015 with tendency of being constant or slightly decreasing with increasing reciprocal d-spacing. By comparison reciprocal peak widths of HMX are significantly higher ranging between 0.005 and 0.03 Å⁻¹, and the values increase until a maximum between 0.25 and 0.3 Å⁻¹ and decrease again for high reciprocal d-spacing.

Figure 3. Williamson-Hall-plots of RDX

Figure 4. Williamson-Hall-plots of HMX

Figure 5. Systematic deviations from linearity for RDX.
The slopes of regression lines fit to the values below 0.3 Å⁻¹ were found to be -0.015(14) and 0.127(23) for RDX (six measurements) and HMX (three measurements), respectively. These values indicate that the micro strain is much higher in HMX than in RDX. Besides, systematic deviations from linearity were found with RDX pointing to anisotropic strain fields (Figure 5). Low values are found for the (hkl)-reflexes with h=2 and l=0, (200), (210) and (220), high values for (111), (002), (102) and (131).

**CONCLUSIONS**

Energetic materials as the nitramines RDX and HMX are relatively low absorbing crystalline materials with low symmetry. Therefore absorption broadening and peak overlap hinder a proper investigation of micro strain using X-ray diffraction evaluated by peak broadening analysis. These problems could be overcome by preparing samples as thin particle layers, which reduces the depths of the diffracting sample volumes. Thus, peaks widths have been reduced e.g. from 0.12 to 0.053°2θ FWHM for RDX.

However, the higher peak resolution is gained at the expanse of intensity. Besides, the preparation and positioning of thin particle layers is already a makeshift technique, and varying layer thickness may influences peak broadening; e.g. different levels of the curves in Figures 3 and 4.

The investigations revealed significant differences between HMX and RDX. The evaluation with Williamson Hall-plot point to higher micro strain in HMX compared to RDX. Considering the defect models described in literature, dislocations in RDX and twins in HMX, it seems that twins have a stronger effect on peak broadening then dislocations. This could be discussed in terms of the different features of these defect types. Strained areas of twins are related to interfaces, whereas areas of dislocations are related to screw or edge like lines. The two-dimensional character of twins may strain a higher portion of crystals than the one dimensional of dislocations. Besides, twin interfaces separate domains and therefore may reduce the size of coherently diffracting crystallites. Not understood is the non-linear nature of the HMX plot, with maximum and decreasing reciprocal peak widths in Figure 4.

A very interesting detail is the anisotropic peak broadening of RDX, particularly measured with the powder layer technique. The RDX peaks (111), (002), and (102) are broadened compared to (200), (210), and (220). Considering edge dislocations, broadening would occur at peaks representing net planes parallel to the edge of a dislocation, but not perpendicular. Starting with low indices [100] or [110] could represent the edge of a dislocation and [001] its burger vector.
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