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Microstructure of energetic crystals – grain by grain via rocking curve

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Abstract. Incorporation of improved particle qualities reduces the sensitivity of plastic bonded explosives. The mechanisms that cause this effect are far from being clear. Therefore the microstructures of the energetic cyclic nitramine RDX have been investigated by means of powder X-ray diffraction, comparing so called reduced sensitivity (RS-RDX or I-RDX) to conventional samples.

The investigations revealed significant differentiations where "best quality" was found with I-RDX followed by RS-RDX and last RDX. The results give evidence to the hypothesis, that the sensitivity of samples is influenced by the microstructure, where size/strain broadening is related to higher sensitivity.

Problems originating from poor orientation statistics of coarse powders have been overcome by measuring rocking curves combined with statistical evaluation. The method gains from information of many crystallites displayed "grain by grain" during rocking the powder sample. Besides, each displayed peak stems from a tiny diffracting volume - the domain -, which reduces peak broadening due to divergence.

The method shall be used for comparison and characterization of the microstructure of coarse powders, where grinding would strongly impact the parameters to be investigated.

Introduction

The microstructure of energetic particles is in the scope of current research. The interest stems from investigations showing that careful processing of crystalline energetic ingredients improves the shock sensitivity of plastic bonded explosives. The mechanisms behind the sensitivity reduction are far from being clear. Particle size, shape, surface morphology, voids, inclusions, impurities, dislocations and twins are discussed to influence the mechanical sensitivity. Besides, broadly feasible methods for distinguishing conventional from reduced sensitivity (RS) products at a crystalline level are required for quality assessment.

X-ray diffraction – state of the art

The use of diffraction line analysis for the investigation of the microstructure is nearly as old as the powder diffractometry itself. In 1918 Scherrer [1] reported that the widths of diffraction lines are inverse to the sizes of crystallites, and 1925 van Arkel [2] found that lines are broadened by micro strain. The line broadening may be evaluated as described by Warren and Averbach [3] and Williamson and Hall [4]. Contrary to conventional powder measurements, where intensity is monitored in dependence of the diffraction angle 2θ, single crystals could be measured by means of rocking curves. Within this technique radiation source and detector are positioned within a reflection condition and the crystal is tilted trough its reflective orientation [5]. The resulting peak widths in terms of the sample angle ω may be used for characterizing crystal quality. Spieß et al. [6] describe the Full Width at Half Maximum *FWHM* β_{rock} of diffraction peaks measured by rocking curves as in equation (1); with the intrinsic half width subscribed by *int*, and the contributions from measuring device *G*, mosaicity *M*, micro strain ε, crystallite size *D* and sample bend *r*. The summation of squares is justified for Gaussian distributions of all effects only.

$$\beta_{rock}^2 = \beta_{\text{int}}^2 + \beta_G^2 + \beta_M^2 + \beta_\varepsilon^2 + \beta_D^2 + \beta_r^2 \tag{1}$$

However, of particular interest for the internal crystal quality are the terms for crystallite size, mosaicity and micro strain. The mosaicity and micro strain terms may be evaluated according to equations (2) and (3); with the dislocation density ρ_V, the magnitude of the Burger vector *b* and the mean square strain ε_{ms}.

$$\beta_M^2 = 2\pi \ln(2) \cdot b^2 \cdot \rho_V \tag{2}$$

$$\beta_\varepsilon^2 = \left[8 \cdot \ln 2\varepsilon_{ms}\right] \tan^2 \theta \tag{3}$$

Application to explosives

Powder X-ray diffraction has proved to be a powerful tool for characterizing explosive crystals; particularly in terms of polymorphism, solid state reactions, thermal expansion or phase interaction [7]. Within the last years approaches were made with the aim to characterize the microstructure of energetic particles by means of line profile analysis [8, 9]. Particularly, the cyclic nitramines RDX ($C_3H_6N_6O_6$) and HMX ($C_4H_8N_8O_8$) have been investigated.

The investigations revealed characteristic line broadening that distinguish different defect types - dislocations in RDX vs. twins in HMX. Moreover, different product qualities of fine HMX and RDX powders have been assessed by measurements at the synchrotron ANKA, and discussed in terms of micro strain and crystallite size. Line profile analysis revealed higher internal crystal qualities of the reduced sensitivity variants RS-RDX and I-RDX compared to the conventional RDX; most likely in terms of larger apparent crystallite size [9]. The method, however, fails if coarse powders have to be investigated, where due to poor orientation statistics jagged line profiles hinder a proper analysis. But the poor orientation

statistic may be converted into an advantage, when reflections from domains are evaluated separately; grain by grain. While measuring a rocking curve, domains are tilted in and out of their reflection conditions, randomly. For a coarse powder and not too many particles, reflections may be separated and evaluated statistically [9].

Experimental and evaluation

Coarse powders of conventional, reduced sensitivity and insensitive RDX with particle sizes about 200 µm have been investigated by means of rocking curves. Measurements were performed on a conventional laboratory Bragg-Brentano Goniometer D5000 from Bruker AXS, equipped with copper tube, vertical soller slits, Ni-Kβ-filter, scintillation counter and at the synchrotron Angström-Quelle Karlsruhe ANKA with a wavelength of 1.3 Å, a Bragg-Brentano Goniometer equipped with a Ge-analyzor crystal. Each sample has been measured at three reflections (111), (200), (002) with the sample tilting from $\omega = \theta$ - 5° to θ + 5° with step width of 0.005 and 0.004°. Symmetric Pearson VII analytical functions were fitted to the diffraction profiles yielding intensities and Full Widths at Half Maximum (FWHM) of each resolvable peak. The peak width distributions were evaluated by plotting the normalized cumulative number of peaks versus peak widths and by determining median peak widths X_{50}.

Results

Figure 1 and 2 show sections of rocking curves measured at the synchrotron with RS-RDX; reflection (111). The rocking curves yield random distributions of reflections that frequently overlap or accumulate to "reflection cluster" as e.g. in figure 1 between 64 and 65 °ω. The decomposition of such clusters by peak fit is shown in figure 2.

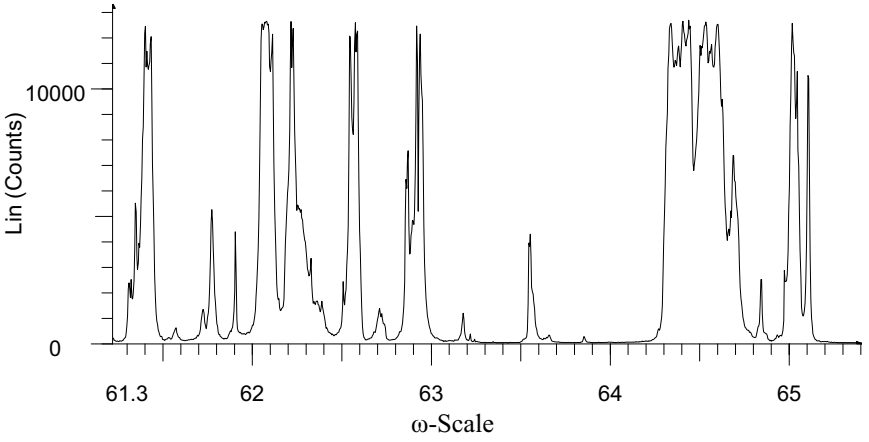

Figure 1. Section of a rocking curve measured with I-RDX at the synchrotron (ω-scale is shifted by 57° due to the Kappa-goniometer offset angle)

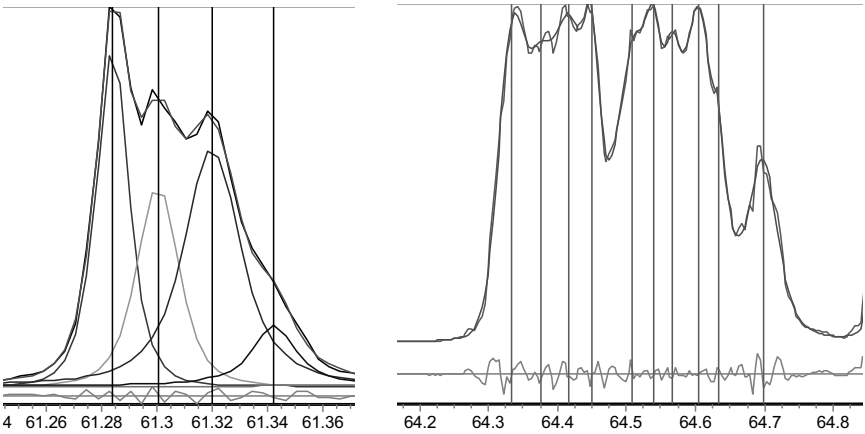

Figure 2. Samples of line profile fits of rocking curve signals (Lin. counts vs. ω-scale shifted by 57°)

The normalized cumulative number of peaks plotted versus peak widths is shown in figure 3, where the left diagram depicts synchrotron and the right laboratory data. Each curve represents at least 260 rocking curve peaks, typically between 300 and 500. The curves in the right diagram intercept the 0.5 level at broader *FWHM* than in the left diagram. Beside this shift, synchrotron and laboratory XRD data are in good coincidence, particularly in terms of the run of the curves and the differentiation of samples.

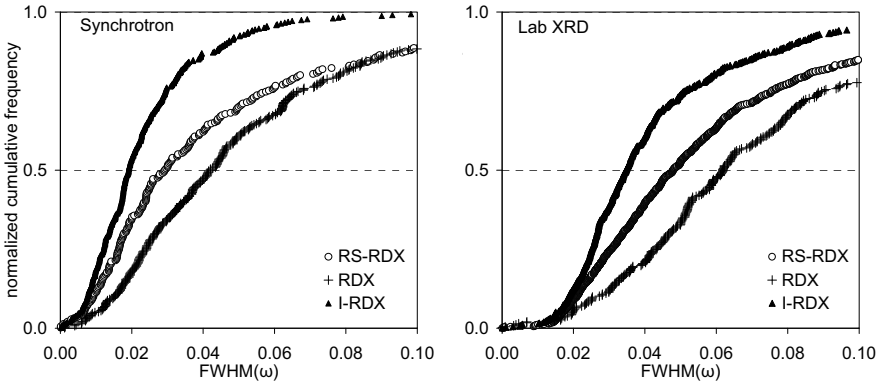

Figure 3. Normalized cumulative number of peaks as a function of peak width, as obtained with Synchrotron radiation (left) and with conventional laboratory XRD (right).

For quantification of the line broadening median peak widths (where 50 % are reached) are plotted in figure 4. Narrow peaks were found for I-RDX with median peak widths of 0.019

(0.033) followed by RS-RDX with 0.028 (0.047) and last the conventional RDX with 0.043 (0.063); results from Lab-XRD are given in brackets. With standard deviations of about 0.006 determined by Lab-XRD [9] the differences proof to be significant.

The investigations of the coarse samples reveal relatively high crystal quality of I-RDX, medium quality of RS-RDX and a comparably poor quality of RDX. They are in coincidence with the investigations of the fine powders that indicate a higher crystal quality of the reduced sensitivity samples (RS-RDX and I-RDX) compared to the conventional RDX [9].

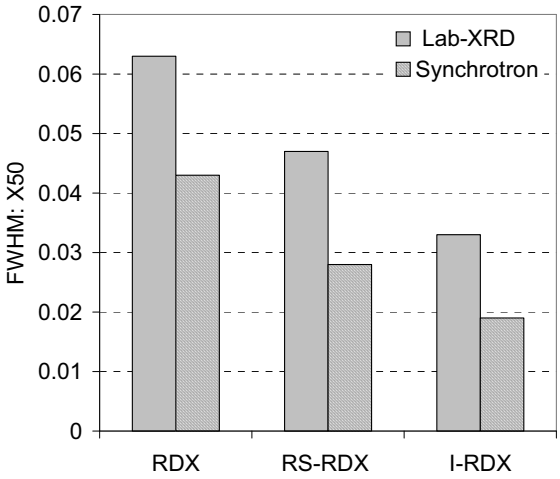

Figure 4. Median peak widths of RDX samples determined by means of rocking curves; high, medium and poor crystal quality of I-RDX, RS-RDX and RDX, respectively.

Conclusions

The investigations show that the microstructure of coarse powders with about 200 µm median particle sizes can be distinguished by measuring rocking curves and statistic evaluation of size/strain line broadening. The method gains from information of many crystallites displayed "grain by grain" during rocking the powder sample.

Besides, each displayed rocking curve peak stems from a tiny diffracting volume - the domain, which reduces peak broadening due to divergence. Thus, measurements with synchrotron and with laboratory XRD revealed same evidence. However, it should be mentioned here that two special measuring systems have been compared, so no general comparison of synchrotron and laboratory XRD could be obtained, nor has been in the scope of the investigations.

The method shall be used for comparison and characterization of the microstructure of coarse powders, where grinding would strongly impact the parameters to be investigated; e.g. crystallite size and micro strain. A more detailed evaluation may include not only the median peak widths but the distribution and the dependence on the lattice spacings.

The investigations of explosives revealed significant differences, where “best quality” (comparably narrow peaks) was found with I-RDX followed by RS-RDX and last RDX. The results give evidence to the hypothesis that the sensitivity of samples is influenced by the microstructure, where size/strain broadening is related to higher sensitivity.

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