Investigation of RS-RDX Samples from the MSIAC-Round Robin by Means of X-ray Diffraction Rocking Curves

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Introduction

The microstructure of explosives is in the scope of current research. The interest stems from investigations showing that careful processing of crystalline ingredients reduces the shock sensitivity of plastic-bonded explosives. The mechanisms behind the sensitivity reduction are far from being clear.

In this context the NATO Munitions Safety Information Analysis Center (MSIAC) organized a Reduced Sensitivity RDX Round Robin (R4) distributing seven coarse RDX-powders ($C_3H_6N_6O_6$) to laboratories all over the world [1, 2]. These samples have been investigated at FhG-ICT and at Empa by means of X-ray Powder Diffraction Rocking Curves in order to correlate micro-structural parameters with shock sensitivities and to verify whether the method would deliver comparable results from different laboratories.

Rocking Curves of Coarse Powders

In the last years approaches were made in order to characterize the microstructure of energetic particles by means of line profile analysis of diffraction patterns, particularly, of the cyclic nitramines RDX ($C_3H_6N_6O_6$) and HMX ($C_4H_8N_8O_8$). [3, 4, 5] The investigations revealed characteristic line broadening that allows distinguishing different defect types - dislocations in RDX vs. twins in HMX. Moreover, different product qualities of fine powders have been assessed by XRD measurements at the synchrotron source ANKA in Karlsruhe, Germany. Line profile analysis revealed higher crystal qualities, in terms of larger crystal sizes and/or lower micro strain levels, of the reduced-sensitivity variants RS-RDX and I-RDX compared to the conventional RDX. The method, however, fails if coarse powders have to be investigated, due to poor orientation statistics. The problem can be overcome by measuring Rocking Curves. [4, 5]

Experimental and Evaluation

Rocking Curves were measured at the FhG-ICT and at Empa on conventional Bragg-Brentano Goniometers D5000 from Bruker AXS, equipped with copper tubes, vertical soller slits, Ni-Kβ-filters and scintillation counters. The samples were measured twice for each reflection (111), (200) and (002), tilting from $\omega = \theta - 5°$ to $\theta + 5°$ with a step width of 0.005°. Symmetric Pearson VII analytical functions were fitted to the diffraction profiles to extract Full Widths at Half Maximum (FWHM) of resolvable peaks. The peak width distributions were evaluated by plotting the normalized cumulative number of peaks versus peak widths and by determining the median peak widths X_{50}. Evaluation of 150 to 500 peaks per sample provides the basis for statistical relevance.

Results

Figs. 1 and 2 depict the normalized cumulative number of peaks obtained at Empa and ICT; here each curve includes data from six measurements. The median (X_{50}) and mean peak widths are summarized in Tab. 1 together with shock sensitivity data and HMX content provided by the MSIAC RS-RDX Round Robin [2].

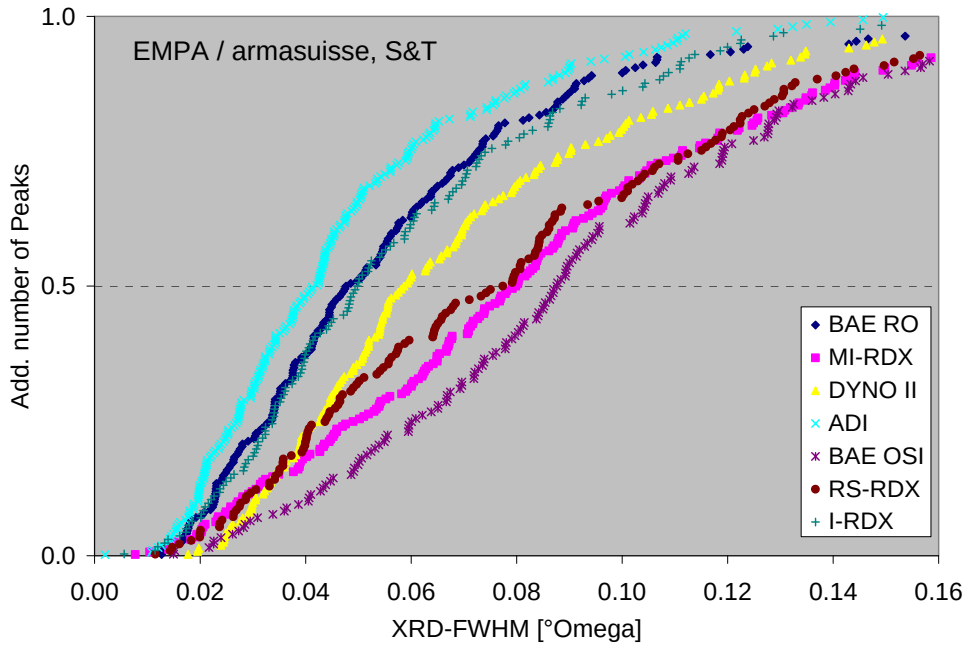

Fig. 1: Normalized cumulative number of peaks in dependence of the peak width (FWHM), measured at Empa

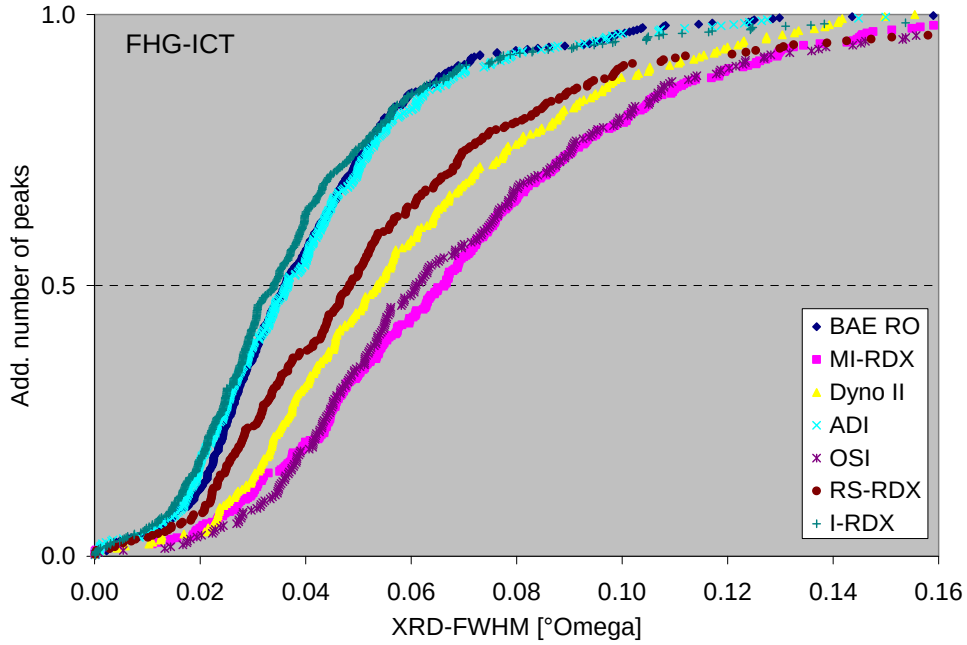

Fig. 2: Normalized cumulative number of peaks in dependence of the peak width (FWHM), measured at FhG-ICT

Both plots show diverging curves representing different RDX-qualities. The FhG-ICT curves are closer and smoother due to the larger number of evaluated peaks. Besides, they are shifted to smaller FWHM compared to the armasuisse, S&T / Empa curves, which may be attributed to geometry and resolution of the measuring systems. The standard deviations of mean and median peak widths in Tab. 1, calculated from six rocking curves, verify significance of different peak broadening. The trend to smaller standard deviations of the ICT data compared to the armasuisse, S&T / Empa data may also correlate with the larger number of evaluated peaks. The results from "sharper peaks", e.g. from RO, I-RDX and ADI, deviate less than those from broadened reflections (OSI, MI-RDX), which may be related to reduced peak overlap of narrow peaks.

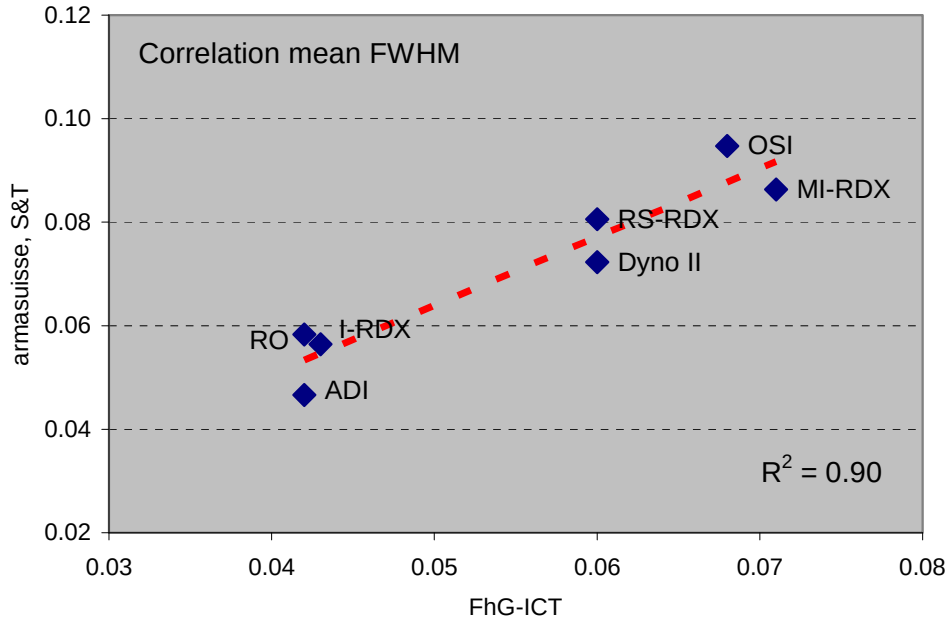

Fig. 3: Correlation of mean FWHM (ø) revealed by armasuisse, S&T / Empa and FhG-ICT

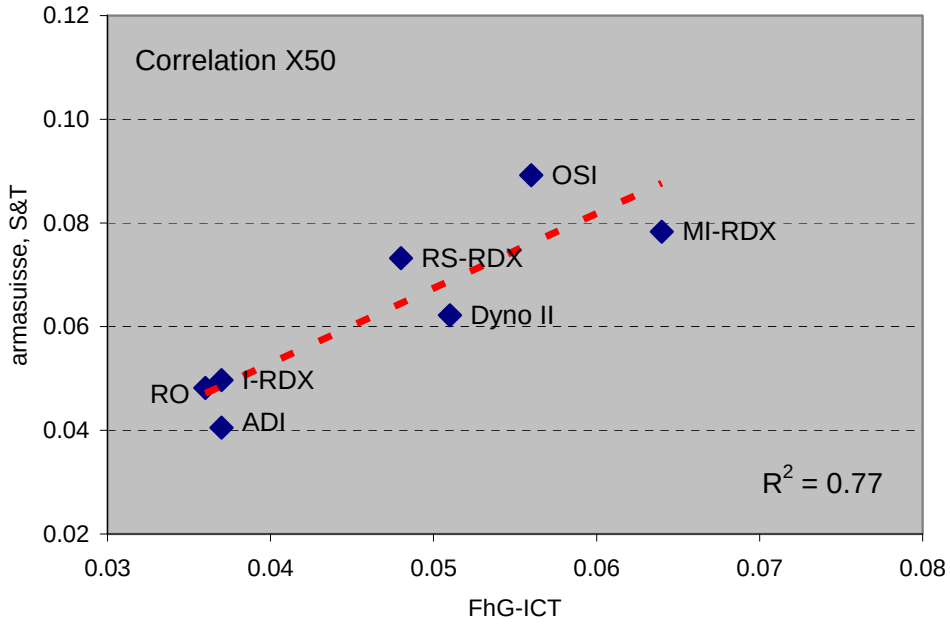

Fig. 4: Correlation of median FWHM (X50) revealed by armasuisse, S&T / Empa and FhG-ICT

The Figs. 3 and 4 correlate results obtained at armasuisse, S&T / Empa with those of the FHG-ICT. Plotting the mean and median peak widths (X_{50}) of the two XRD laboratories one another, yields good correlations with correlation coefficients of 0,77 and 0,90 for the median and mean FWHM, respectively. There are, however, inconsistencies, as in the ranking from narrow to broad peaks, Dyno II interchanges with RS-RDX and OSI with MI-RDX, when data from armasuisse S&T / Empa are compared to those from FhG-ICT.

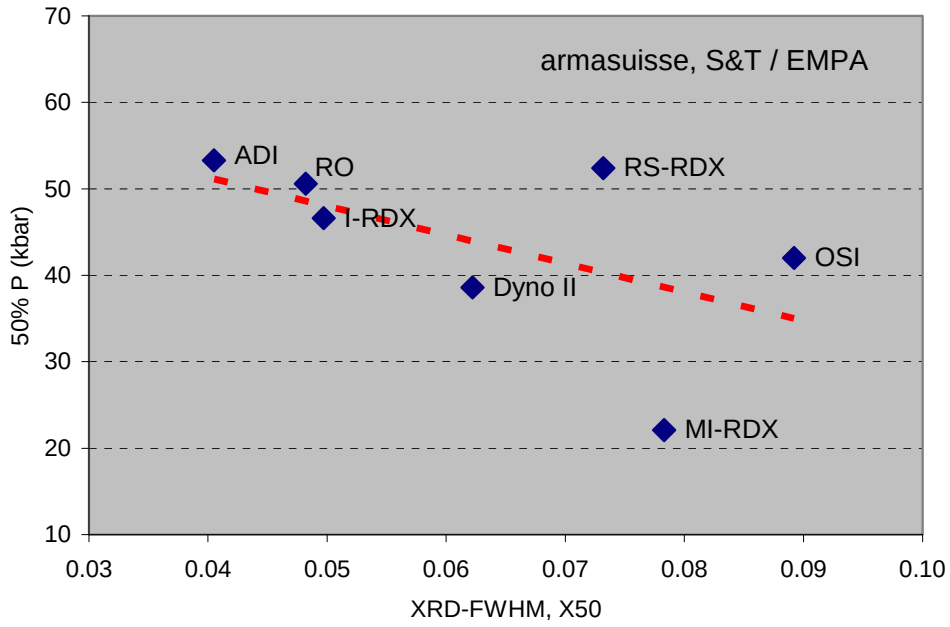

Fig. 5: Correlation of the initiation pressure of Large Scale Gap Tests LSGT [1] with the median peak width of XRD Rocking Curves measured at Empa

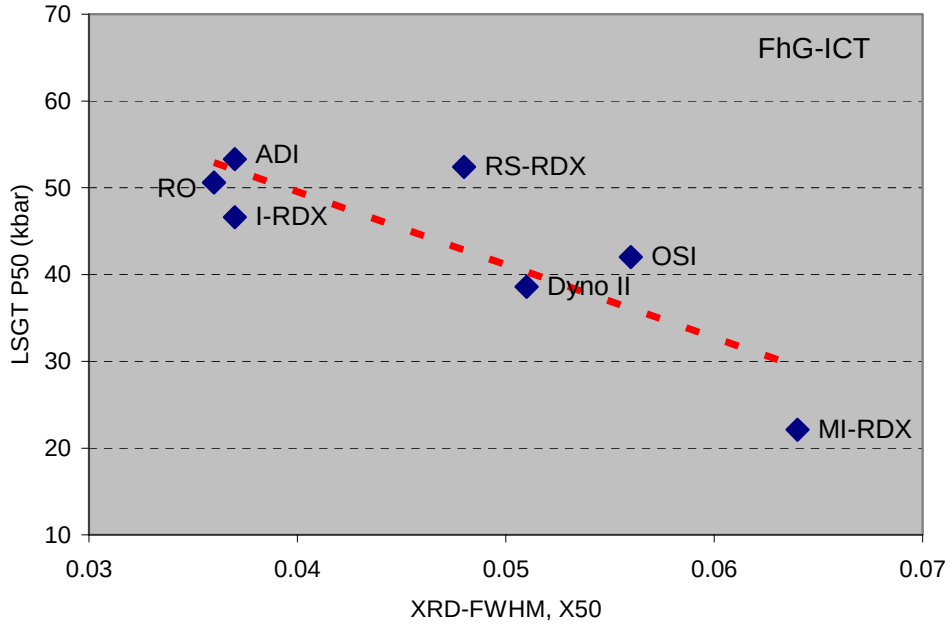

Fig. 6: Correlation of the initiation pressure of Large Scale Gap Tests LSGT [1] with the median peak width of XRD Rocking Curves measured at ICT

The Fig. 5 and 6 correlate the shock sensitivity with the peak broadening obtained by Empa / armasuisse, S&T and FhG-ICT, respectively. The plots separate the reduced

sensitivity varieties ADI, I-RDX and RO at the left upper part of the diagram; at relatively narrow peaks and high initiation pressures. The sensitive varieties OSI and MI-RDX occur on the right and lower part of the plots, indicating significant size/strain broadening combined with a relative low initiation pressure. The Dyno samples (RS-RDX and Type II) range somewhere between.

So far the results revealed the low pressure-sensitive products have a large grain size and/or a low micro strain level, while the sensitive materials are composed of smaller coherent grains and/or high micro strain. Both measurement series at FhG and Empa show this trend unambiguously.

However, the sample RS-RDX doesn't comply with this relation as it represents reduced shock sensitivity combined with significant peak broadening. The HMX content in Tab. 1 may give an idea about this outstanding position of RS-RDX in the plots. The very low concentrations of ADI, RO-BAE and I-RDX do not affect peak broadening nor shock sensitivity, whereas high concentrations in BAE-OSI and Dyno II affect both. The concentration of the sample RS-RDX lies between in a range where broadening is already affected but not yet sensitivity. In this concept MI-RDX adopts the outstanding position, showing that a low HMX concentration is a crucial but not a sufficient condition for low shock sensitivities nor relatively high crystal qualities in terms of size/strain-broadening.

Tab. 1: Data obtained by XRD-Rocking curves at armasuisse, S&T / Empa and FhG-ICT, and from the MSIAC-RS-RDX-Round Robin [1].

	GAP Test [1]		XRD peak width as FWHM				HMX
	P	Cards	ICT [2]		armasuisse, S&T/Empa		content [1]
	(kbar)		X_{50}	ø	X_{50}	ø	[%]
ADI	52.1	114	0.037(6)	0.042(1)	0.041(2)	0.047(4)	0.02(1)
RO BAE	50.6	118.5	0.036(3)	0.042(3)	0.048(6)	0.058(9)	0.19(13)
I-RDX	46.6	131	0.037(6)	0.043(6)	0.050(8)	0.056(8)	0.02(8)
D. RS-RDX	52.4	113	0.048(3)	0.060(8)	0.073(21)	0.081(16)	0.82(10)
BAE OSI	42	144.5	0.056(10)	0.068(9)	0.089(9)	0.095(10)	7.36(92)
MI-RDX	22.1	194.5	0.064(10)	0.071(5)	0.078(12)	0.086(14)	0.03(2)
Dyno II	38.6	150.5	0.051(6)	0.060(3)	0.062(9)	0.072(6)	8.55(228)

Standard deviations are given in parentheses in terms of the last digit.

Summary

XRD rocking curves combined with statistic evaluation are a promising technique for quality assessment of coarse explosive powders. A set of seven different Reduced Sensitivity RDX-samples materials by MSIAC has been tested at two X-ray diffraction laboratories, Empa and the Fraunhofer ICT. The comparison of data from the two laboratories yielded a moderate good correlation and significant differences of crystal qualities. So far, the investigations give evidence to reproducibility and resolution of this technique.

Detailed evaluation and correlations of the data revealed that structure parameters such as crystallite size, micro strain and HMX content correlate with the shock sensitivity of RDX. The reduced sensitivity variants ADI, RO and I-RDX combine narrow diffraction peaks with high purity and HMX content below 0.2 %. A slightly higher impurity of 0.8 % HMX disturbed the crystal perfection but didn't affect the reduced sensitivity, as shown by the

sample RS-RDX. Much higher HMX contents strongly interfere with both crystal perfection and shock sensitivity in the samples OSI and DYNO II.

Thus, it seems obvious that HMX impurities of a few percent sensitize RDX. An inverse conclusion, saying that pure RDX leads to reduced sensitivity and/or more perfect crystals, is not valid as shown by the sample MI-RDX. This sample contains only 0.3 % HMX but strongly broadened diffraction peaks, indicating poor crystal quality. This means that pure RDX may help gaining reduced shock sensitivity, however, only when prepared through careful crystallization processes.

Acknowledgement

The Naval Surface Warfare Center and the NATO Munitions Safety Information Analysis Center is gratefully acknowledged for organizing the RS-RDX-Round Robin and providing well characterized RDX samples; namely Ruth Doherty and Duncan Watt.

References

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