MICROSTRUCTURE OF THE PLASTIC BONDED EXPLOSIVE KS32

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ABSTRACT

Plastic bonded explosives are highly filled polymers containing up to 90% high energy crystalline solid loads. Different non-destructive diffraction techniques such as rocking curve imaging were applied in order to characterize the microstructure and ingredients of PBX KS32, including its behavior in shock-loading tests. The investigations revealed a significant change in the amorphous binder, as well as damages to the embedded coarse HMX crystals during shock-loading.

INTRODUCTION

Plastic-bonded explosives (PBX) are highly-filled polymers containing up to 90% high energy crystalline solid load. The high loads are reached using bi- or poly-modal particle size distributions, in which smaller particles fill the gaps between the larger ones. In recent years, the microstructure of the solid ingredients came under the scrutiny of research when it was discovered that incorporating meticulously recrystallized particles reduces the shock sensitivity of PBXs. In such a context, factors such as particle size, shape, surface morphology, voids, inclusions, impurities, dislocations and twinning have been discussed to influence the mechanical sensitivity and the creation of hot spots during shock-loading. The crystallite size and microstrain of high explosive powders were investigated by means of laboratory and synchrotron X-ray diffraction (Herrmann et al., 2005a, 2005b, 2009a, 2009b). The investigations not only revealed anisotropic diffraction peak broadening, but also correlated size/strain broadening with particle processing and shock sensitivities.

For applications in penetrators, insensitive high explosives (IHE) are required in order to survive heavy mechanical loading, e.g. during supersonic penetration of concrete or rock (Arnold, 2005a,
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Thus investigations were started with the aim to show how the microstructure of the embedded crystals in the PBX KS32 is affected by shock-loading. However, the simultaneous characterization of the ingredients in such a composite remains a challenging task, as it includes a coarse and a fine crystal fraction of the same species, as well as the amorphous binder.

EXPERIMENTAL

KS32 consists of 85% HMX (C₄H₈N₈O₈), a crystalline high explosive, and 15% cured hydroxy-terminated polybutadiene (HTPB) as the binder, with a total density amounting to 1.6 g/cm². The PBX was shock-loaded at MBDA-TDW in Schrobenhausen, Germany, and two loaded samples were investigated at Fraunhofer ICT together with a pristine reference sample. Each sample was measured twice on different surfaces. Figure 1 shows a cut sample as used for the measurements. In order to collect separate information on each ingredient or individual fractions, different XRD measuring and evaluation techniques were applied. Measurements were performed on a Bragg-Brentano Diffractometer D8 Advance from Bruker AXS, equipped with a copper tube, secondary monochromator, scintillation counter and sample changer.

Figure 1. PBX-sample as measured. Cut surface dimensions are approximately 1 cm × 1 cm.
An initial view of the crystalline fractions (HMX) was obtained from 2θ scans evaluated by whole-pattern fitting included in the program system TOPAS from Bruker AXS. The evaluation was based upon the crystal structure data of HMX reported by Choi and Boutin (1970). The evaluation yielded the unit-cell parameters, crystal density and the mean crystallite size $C_{\text{cry size}}$ ($L$) (Balzar, 1999; Bruker, 2008).

The microstructure of the coarse fractions was probed by rocking curves combined with a statistical evaluation (Herrmann et al., 2005b, 2007, 2008). The detector was therefore fixed at selected peak positions and the samples were rocked around their symmetric orientations with a step width of 0.01°$\omega$ and a measuring time of 5 s. The rocking curve patterns were decomposed by means of peak fit using symmetrical Pearson VII functions, and the cumulative numbers of peaks were then plotted against the peak widths of the rocking curve profiles. The run of the curves and the median peak widths ($X_{50}$) were interpreted as a quantity related to the internal state of the crystals.

The amorphous parts were probed by peak fitting 2θ scans, including the run of the base line of the patterns. The amount of the amorphous content $C_{\text{amorphous}}$ was estimated from the relation of the areas $A$ under the halos and the crystalline peaks as related in the following equation:

$$C_{\text{amorphous}} = \frac{A_{\text{halos}}}{(A_{\text{peaks}} + A_{\text{halos}})} \times 100.$$  

RESULTS

The results of the measurements are summarized in Table 1 together with standard deviations estimated from the four measurements of the loaded samples.

Fig. 2 shows 2θ scan sections of two pristine KS32 samples. It should be noted that high intensity fluctuations and jagged profiles occur due to the relatively coarse HMX crystals and their poor orientation statistics, hindering a proper evaluation by whole-pattern fitting. Thus, the results of the whole-pattern fitting yield only an initial assessment of the microstructure.
Table 1: Results of diffraction experiments on two loaded KS32 samples compared to a pristine reference. Values of two measurements for each sample are below, along with the average values and estimated standard deviations $\sigma$.

<table>
<thead>
<tr>
<th>KS32 sample</th>
<th>$C_{\text{amorph}}$ [%]</th>
<th>Cry size L [nm]</th>
<th>Density [g/cm$^3$]</th>
<th>$RC_{X_{50}}$ [$^\circ$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine</td>
<td>17.9 / 15.2</td>
<td>122.8 / 114</td>
<td>1.897 / 1894</td>
<td>0.085</td>
</tr>
<tr>
<td></td>
<td>$\sigma$ 16.6</td>
<td>118.4</td>
<td>1.896</td>
<td></td>
</tr>
<tr>
<td>loaded I</td>
<td>8.3 / 8.6</td>
<td>91.8 / 97.6</td>
<td>1.894 / 1.89</td>
<td>0.148</td>
</tr>
<tr>
<td>loaded II</td>
<td>9.1 / 10.8</td>
<td>77.1 / 91.6</td>
<td>1.892 / 1.892</td>
<td>0.127</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>9.2</td>
<td>84.4</td>
<td>1.892</td>
<td></td>
</tr>
<tr>
<td>$\sigma$</td>
<td>1.1</td>
<td>8.7</td>
<td>0.0016</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. Sections of the $2\theta$ scans of two pristine KS32 samples. The patterns show high intensity fluctuations and jagged peak profiles.

The whole-pattern fitting yielded densities of the incorporated HMX of 1.896 g/cm$^3$ for the pristine sample and a slightly smaller density of 1.892 g/cm$^3$ for the loaded samples. The values are well-distributed around the literature value of 1.894 with an estimated standard deviation of...
0.002 g/cm³, an insignificant difference well within experimental error range. The apparent crystallite size *Cry size L* reduces from an average value of 118.4 to 84.4 nm upon loading, which is considered significant, as the size had shifted more than three times the standard deviation value of 9 nm.

Figure 3. Magnification of the 2θ scan background of a pristine KS32 sample (black) and two loaded samples (blue and red). A halo occurs around 19° 2θ, but with reduced intensity in the loaded samples.
Figure 4. Reference measurement of the binder HTPB (liquid).

An interesting detail was found by magnifying the background. A halo occurs around 19°2θ (Fig. 3). The reference pattern in Fig. 4 shows that the halo belongs to the binder HTPB. After loading of KS32, the intensity of the halo decreased significantly. The concentration of amorphous HTPB, calculated from the areas under halos and peaks, reduced from 16.6 to 9.2%. The binder concentrations of the pristine samples are acceptably close to the expected value of 15% of KS32, even without calibration. The decrease of the amorphous content of the binder is not yet understood, but one possible explanation is the partial crystallization of the binder during shock-loading.

Figure 5. Sections of a rocking curve of KS32 and pattern decomposition.
Figure 5 shows a section of a rocking curve of a KS32 sample and its pattern decomposition using symmetrical Pearson VII profiles. As the x-ray source and the detector are fixed in a reflection position during the rocking curve measurements and only the samples are tilted, large crystallites randomly come into reflection like differently oriented single crystals. Thus, up to 420 peak widths (full widths at half maximum) per sample were obtained and evaluated statistically. The cumulative number of peaks was plotted versus peak width (Figure 6).

The plots show significant differences. The curves of the loaded samples are drawn to higher peak widths indicating damage to the coarse HMX crystals after shock-loading. A quantification of these changes is given by the median peak width $X_{50}$ which is shifted from $0.085^\circ$ for the pristine samples to $0.148$ and $0.127^\circ$ for the loaded samples I and II, respectively. As the coarse crystalline fraction is considered to dominate the sensitivity of a PBX, the rocking curve method reveals crucial information on the microstructure of KS32.

![Figure 6. Cumulative number of rocking curve peaks as a function of the peak width.](image-url)
CONCLUSION

Various non-destructive diffraction techniques were applied in order to characterize the microstructure of the PBX KS32 and its behavior upon shock-loading. The investigations revealed a significant change in the amorphous binder concentration and a consequent damage to the embedded coarse HMX crystals. Further investigations are in progress with a focus on advanced sample preparation, a differentiation of defect types such as twinning and fracture, the structural changes of the binder HTPB, and a separate characterization of the fine HMX fraction in the PBX.

REFERENCES