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THE EVOLUTION OF MICROSTRUCTURAL CHANGES IN PRESSED HMX EXPLOSIVES *

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Recently developed techniques for investigating the microstructure of plastic-bonded explosives have been applied to HMX explosives pressed to various levels of porosity. Microstructural changes in PBX 9501 are followed from the early stages of prill consolidation through typical density to very low porosity (0.6%). As porosity is reduced, the following sequence is observed. Large inter- and intra-prill voids are eliminated with first damage to HMX crystals occurring at prill boundaries. This is followed by increased incidence of crystal twinning and cracking. At the lowest porosities, spall pullout artifacts are observed, cracks associated with particle contact points are more obvious, and the results of intercrystalline indentation or intergrowth migration processes are apparent. A comparison is made, at lowest porosities achieved, with PBX 9404 and X-0242 (a formulation like PBX 9501 with higher binder volume). Possible implications on porosity trends in shock sensitivity data are discussed.

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INTRODUCTION

The quest to identify microstructural features responsible for the nucleation of hot spots in the initiation of high explosives has gone on for several years. Many studies have been conducted on porous[1] and composite explosives to examine the effects of such parameters as particle size, intergranular void size, intragranular crystal defects, binder quantity, and viscoplastic binder properties. Several of these variables frequently correlate with some measure of sensitivity.

As early as 1961, Campbell, et al.[2] reported shock initiation experiments on pressed charges of plastic-bonded HMX in which the sensitivity decreased rapidly as the limiting density was approached. Today, Gustavsen[3] is exploring an apparent variance in shock sensitivity with pressing method (isostatic versus uniaxial die) and density for PBX 9501. Recent unpublished experiments by Dick[4] also indicate that PBX 9501 with slightly lower porosity requires a stronger shock to achieve reaction.

Recently, the efforts of Borne,[5,6] Lefrançois,[7] and van der Heijden[8] have correlated HMX crystal characteristics with shock sensitivity in model laboratory formulations containing 20 - 30 weight percent binder. In parallel with these "structure-property" efforts, several researchers are also developing "process-structure" models for the evolution of microstructural features and as a function of loading conditions.[9,10,11]

This paper presents experimental results on the effect of quasi-static, uniaxial compaction on the microstructure of HMX-based, plastic-bonded explosives with 8 weight percent binder or less. We describe pressing experiments on three different explosives, including two whose shock initiation characteristics have been extensively studied. Commercial powders were purchased and formulated by standard production methods. Pressing conditions were adjusted to control porosity over the range of 0.3% to 21%. The structures of these samples were characterized by several methods, particularly to identify changes in microstructure which might influence shock sensitivity. Evidence from the literature suggests that shock initiation is rather sensitive to small changes in porosity at low porosities. This is attributed to changes in damage resulting from the processing technique. In this study, we identify several features of the pressing damage and relate this damage to porosity.

Several complementary techniques were employed in order to thoroughly characterize these materials. Polarized Light Microscopy (PLM) is the principal tool used in this study, supplemented by Scanning Electron Microscopy (SEM), and small angle neutron scattering (SANS).

The three formulations studied, PBX 9501, PBX 9404, and X-0242, all contain the same specification for original HMX, always incorporating a bimodal particle size distribution. PBX 9501 contains, by weight, 95% HMX, 2.5% estane 5703 (a polyurethane binder) and 2.5% bis-dinitropropyl acetal/formal (a nitroplasticizer). PBX 9404 is 94% HMX, 3% nitrocellulose, and 3% choloroethyl phosphate (a plasticizer). There is an abundance of shock sensitivity data in the literature for both PBX 9501 and especially for PBX 9404 at various levels of porosity, much of which is reviewed by Howe[12] in these proceedings. X-0242 has the same constituents as PBX 9501 but a greater proportion of binder (92% HMX, 4% estane, 4% nitroplasticizer). This allowed us to more easily observe the binder and to consolidate to a lower porosity than could be achieved with the PBX 9501.

EXPERIMENTS

Molding powder granules, or prills, of PBX were prepared using the standard slurry process. For PBX 9501 and PBX 9404 this was done commercially by Holston Defense Corporation (lots HOL 87L730-009 and HOL 89C730-010 for PBX 9501 and 620-5 for PBX 9404). The X-0242 was prepared locally as Blend 88-03. Samples were consolidated by uniaxial pressing in a cylindrical steel die as elaborated below. Porosity was estimated by measuring the bulk density of the pressed piece and comparing that with reported theoretical maximum densities for the composite explosives (1.860 g/cm^3 for PBX 9501, 1.832 g/cm^3 for X-0242, and 1.865 g/cm^3 for PBX 9404).

Microstructural examination was performed on pieces of each sample cut near the center of the compact in order to avoid skin effects. Density (and hence, porosity) was not measured for the individual sub-samples. Polarized light microscopy was conducted by mounting material in a low-viscosity epoxy, polishing the cured mount, examination in reflected light and photography by digital CCD camera as described by Skidmore, et al.[13]

The study of PBX 9501 was conducted in two phases. The first set of experiments used lot HOL 89C730-010 molding powder pressed in a fixed volume mold (approximately 41 mm diameter, 55 mm high). All samples were pressed with 20,000 psi (138 MPa) on the mold and the material at 90°C, except one which was intentionally pressed at ambient temperature. Porosity was estimated using a geometric method to determine bulk density since the high porosity of some pieces precluded typical determination by immersion methods. Porosities for this group of samples ranged from 21% to 1%. (A typical PBX 9501 component is pressed to 1-2% porosity.)

The second set of PBX 9501 experiments focused on densities higher than typical (i.e. lower porosities). Material from lot HOL87L730-009 was pressed at 90°C. Pressure applied to the material (open setup, approximately 25 mm diameter, 25 mm high) was 38,000 psi (262 MPa), resulting in porosities of 2, 0.9, and 0.6% (corresponding densities of 1.822, 1.843, 1.848 g/cm^3). We were unable, in these studies, to achieve density above 1.848 g/cm^3. Porosities were determined using immersion density measurements on these high density samples.

Samples of PBX 9404 were prepared (approximately 25 mm diameter, 25 mm high) at porosities of 8, 1, 0.6% (corresponding densities of 1.718, 1.843, 1.854 g/cm^3) by pressing the material at 80°C and 30,000 psi (207 MPa). In this material, however, an apparent incompatibility of binder constituent(s) and the epoxy mount obfuscated the PLM examination for all but the lowest porosity sample.

A high density sample of X-0242 (0.3% porosity) was prepared (approximately 25 mm diameter and 25 mm high) using heat and pressure. The higher fraction of binder made it possible to achieve this low porosity.

The theory and experimental technique for small angle neutron scattering were previously reported by Mang, et al.[14] This paper includes the results on the coarse and fine grades of HMX as loose powders and pressed pieces. The HMX powders are typical of those used in the PBXs studied in the present work. The coarse grade was pressed to 93% theoretical maximum density (7% porosity), which corresponds to the volume percentage of HMX in PBX 9501. The fine grade was pressed to 10% porosity.

RESULTS AND DISCUSSION

The structures of the first set of PBX 9501 samples (high to nominal porosity) are shown in PLM and SEM in Figures 1 through 8. These show that the deformation path, like the starting material, is quite heterogeneous and with the mixed "fines and binder" constituent sustaining the majority of the plastic strain early in the pressing cycle, while the harder, coarse HMX crystals are significantly strained later.

Figure 1. shows a SEM view of the surface of a molding powder granule which shows a qualitative measure of the heterogeneity of distribution of "fines and binder" at the particle surface. Observations of polished sections of molding powder by Skidmore, et al.[13] have shown that internal voids within the prills are similarly decorated with fines, though the polished section results are somewhat clouded by the chemical interaction of the mounting medium with the binder.

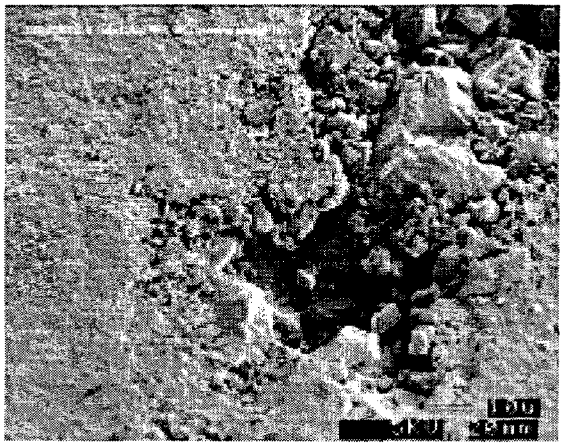

FIGURE 1. PBX 9501 MOLDING POWDER GRANULE SHOWING TYPICAL PREVALENCE OF FINE PARTICLES MIXED WITH BINDER AT SURFACE.

Figure 2. shows an SEM view of PBX 9501 hot-pressed to 16% porosity which has been cut with a diamond saw. While the contrast conditions here do not support discrimination between coarse HMX crystals and "fines and binder", the distribution of apparent void space does support the important conclusion that the early stages of consolidation are accomplished predominantly by the rearrangement of prill boundaries to consume free volume between the prills. This conclusion is further supported, with additional detail on the preservation of the coarse crystals, in polarized light in Figure 3.

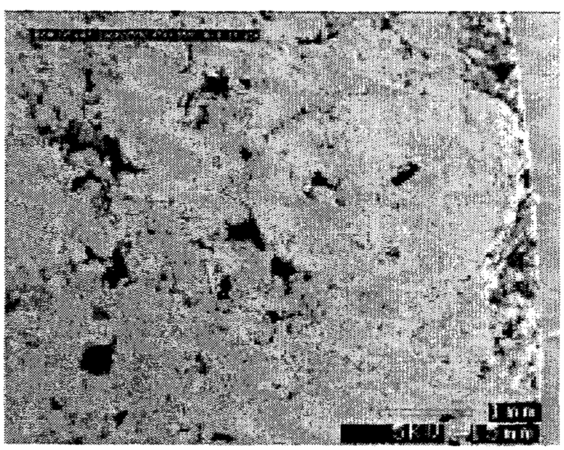

FIGURE 2. PBX 9501 HOT PRESSED TO 16% POROSITY, DIAMOND-SAW CUT AND VIEWED BY SECONDARY ELECTRON IMAGING IN SEM.

FIGURE 3. PBX 9501 HOT PRESSED TO 16% POROSITY, EPOXY-MOUNTED, POLISHED AND VIEWED BY PLM.

The consolidation of samples to high densities is a far more constrained process, and the coarse crystals are required to contribute plastic strain as well as the binder. This they do poorly, using the limited mechanisms of twinning and microcracking available to them at near-ambient conditions. A typical crack array is shown in Fig. 4.

On the other hand, the special role of prill boundary sliding can be traced, albeit with increasing difficulty, into materials of nominal density. Figure 5 shows the same area as Figure 4 in a sample pressed to 2% porosity at ambient temperature. Figure 3 is focused on the top surface. By changing the plane of focus slightly in Fig. 5, we can identify vestigial prill boundaries. The black/white sense of the contrast is Fresnel-like and can be reversed by change of focus as shown in the micrographs. Several factors in the sample preparation combine to decorate the prill boundaries for this observation including potentially preferential access to the epoxy, relief during polishing due to their high loading of fines, and stress relaxation after polishing.

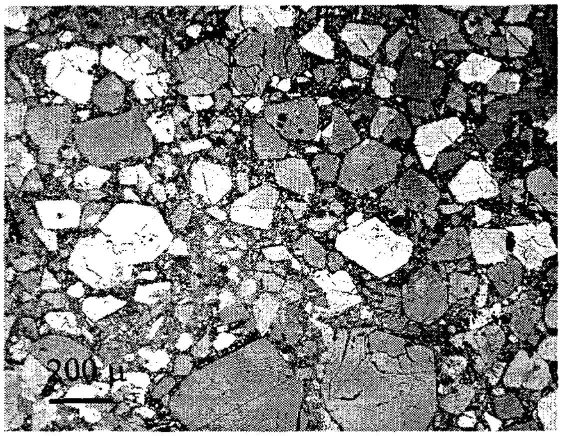

FIGURE 4. PBX 9501 PRESSED AT AMBIENT TEMPERATURE TO 2% POROSITY, FOCUS ON SURFACE DETAIL.

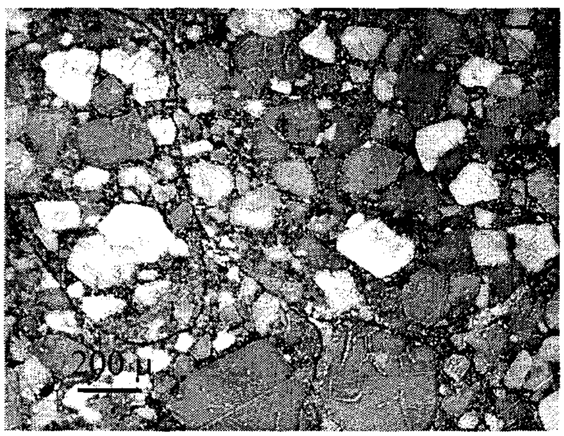

FIGURE 5. PBX 9501 PRESSED AT AMBIENT TEMPERATURE TO 2% POROSITY, FOCUS PLANE ADJUSTED TO HIGHLIGHT PRILL BOUNDARIES (SAME FIELD AS FIGURE 4.)

Figure 6. provides a more highly resolved view of a prill boundary in PBX 9501 hot pressed to 21% porosity. Examination of Figure 7. shows that fracture of large HMX crystals occurs primarily in prills which undergo extensive deformation. Under conditions of partial densification, prill deformation is not uniform, and localized regions of high fracture result. As densification is increased, more and more prills are significantly deformed and fracture becomes more extensive.

FIGURE 6. PRILL BOUNDARY IN PBX 9501 HOT PRESSED TO 21% POROSITY

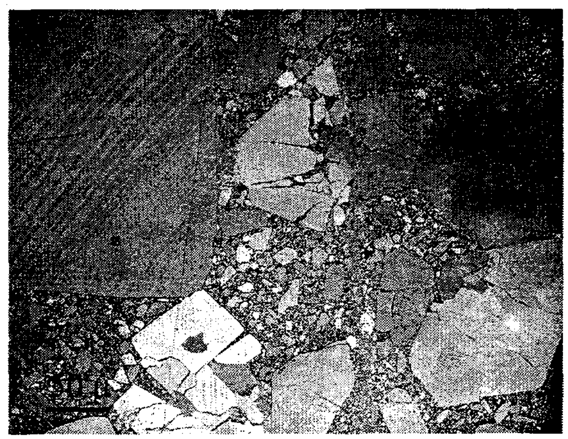

FIGURE 7. PRILL BOUNDARY IN PBX 9501 HOT PRESSED TO 7% POROSITY

In the large HMX crystals themselves, transgranular microcracking and twinning were observed to occur more frequently as porosity was reduced. Figure 8 is a PLM micrograph of PBX 9501 pressed to 1% porosity which shows evidence of processing-induced twinning and crack formation. Note also the presence of a modest density of intragranular voids and crystalline intergrowths. Such features may serve as foci for processing-induced fracture.

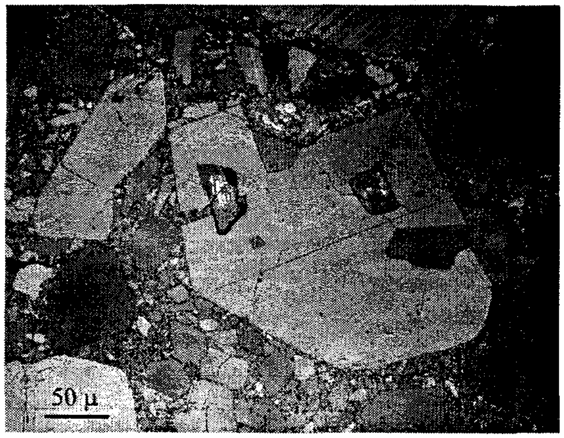

FIGURE 8. PBX 9501 HOT PRESSED TO 1 % POROSITY.

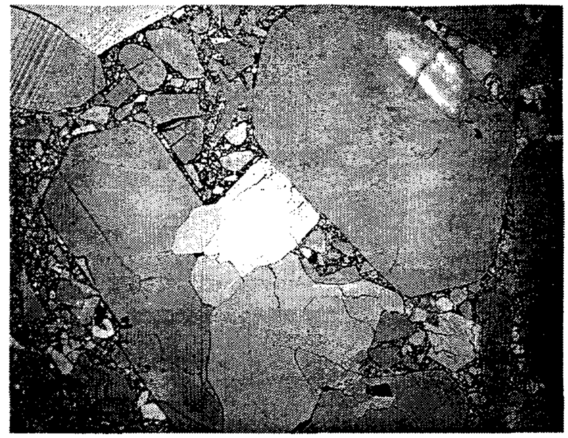

FIGURE 9. INDENTATION AND CRACKING OF HMX CRYSTALS IN PBX 9404 HOT-PRESSED TO 0.6% POROSITY.

We note here that the 10% - 1% porosity regime, while rich in structural evolution, is also a regime in which shock properties vary quite little with porosity. Thus these interesting defect distributions are not likely to directly control the distribution of hot spots or the initiation properties of the explosives.

The second set of samples were prepared from all three materials at porosity 1% and below, where the initiation properties for the most extensively studied systems do show dependence on density. PBX 9501 and PBX 9404 behave similarly in this regime and will be discussed together.

A non-representative but particularly instructive region from high density PBX 9404 is shown in Figure 9. Here we see three large grains, presumably part of a "stress chain" of hard crystals severely loaded during pressing. The central grain is compressed under significant constraint without cracking at its left and likewise compressed without support, and with copious cracking, on its right. The "anvil" crystal at the right shows a bright out of focus reflection due to a subsurface crack. Three noteworthy aspects of this behavior – the apparent indentation of one crystal by another under the influence of applied stress and hardness anisotropy, the accumulation of high crack density in the coarse crystals, and the increasing incidence of out of plane vent cracks - recur in high density samples of both PBX 9501 and PBX 9404. The apparent flow lines in the central grain also suggest, for this specific site, shear displacement while under pressure.

The three dimensional linkage of these intragranular microcracks poses a new problem in microscopic interpretation. Patches of material isolated by these crack arrays become functionally non-bonded to the sample and are very difficult to preserve intact through sample polishing. We term these defects "spall pullout artifacts", shown in Figure 10. Recognizing the increasing prominence of networked cracks in the highest density samples, we cannot tell what becomes of the intragranular porosity left over from the molding powder after the highest pressure pressing. The increase in spallation more than compensates for any decrease in real porosity apparent in the microscope.

FIGURE 10. SPALL PULLOUT ARTIFACTS FROM PBX 9404 HOT-PRESSED TO 0.6% POROSITY.

These low porosity samples show a markedly higher level of cracking associated with particle-to-particle contact points. Figure 11 shows several examples of this. It is not clear whether these are always associated with a prill boundary.

The increasing incidence of crystal-to-crystal indentation is also noteworthy in this regime. These observations, though, include two groups of phenomena, since the crystal-within-crystal intergrowths observed in the molding powder could be squeezed out just as well as the outside indenter crystals are squeezed in. While the indentation from the outside requires only hardness anisotropy and the externally imposed pressure, the driving force for the ejection of once occluded crystals is less obvious. Still, the density of fully occluded intergrowths does seem to decrease. The right side of Figure 11 shows a typical, modified intergrowth in low porosity PBX 9501.

FIGURE 11. CRACKING OF LARGE CRYSTALS AT PARTICLE CONTACT POINTS IN PBX 9501 HOT PRESSED TO 0.6% POROSITY

The high-binder material, X-0242, behaves differently during high pressure pressing. Figure 12 shows a typical field of view, in which increased density of "fines and binder" is readily apparent as the wide dark network surrounding the coarse particles. The coarse particles are still twinned, but they are not fractured to nearly the extent observed in the 5-6% binder systems. This was the most dense sample we were able to consolidate during the entire study at 0.3% pores.

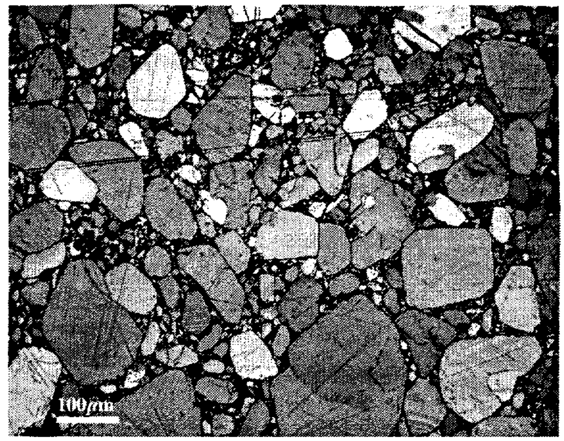

FIGURE 12. X-0242 (HIGH BINDER VERSION OF PBX 9501) HOT PRESSED TO 0.3% POROSITY

Finally, we applied small angle neutron scattering (SANS) to measure pore size distributions in binderless HMX. As summarized in Figure 13., the apparent pore size decreases rapidly in pressed samples, suggesting that the large intragranular pores are effectively squeezed out.

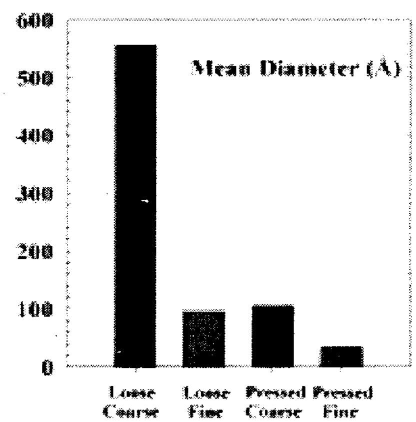

FIGURE 13. SMALL ANGLE NEUTRON SCATTERING DATA FOR POROUS HMX

We were unable to associate trends in processing-induced changes in the microstructure with changes in sensitivity. Howe[12] showed that the threshold for initiation under conditions of long duration planar shock loading increases at very low porosities but becomes independent of porosity at lower densifications. The decrease in shock sensitivity associated with very low porosity may be due to elimination of intragranular voids, but this has yet to be demonstrated. One very strong trend observed in the PBX 9501 samples was the occurrence of extensive microfracture with increasing densification.

Increasing the binder content (X-0242) allowed pressing to very low porosities without significant microfracture. Steele, et al.[15] determined that the shock sensitivity (as measured by the large scale gap test) for X-0242 with 8% binder was significantly lower than for PBX 9501. This may be due to the reduced microfracture, or it may be due to reduced porosity (the X-0242 samples had 0.3% porosity, versus the 0.6% for PBX 9501). Other shock initiation experiments with X-0242 at 0.6% porosity are planned.

Idar, et al.[16] reported that low porosity PBX 9501 exhibits a lower threshold for initiation by low velocity impact than does PBX 9501 with greater porosity. Low velocity impact initiation under the conditions studied is believed to be caused by localized shear deformations. It may be that the reduced porosity changes the conditions for shear localization. However, this is entirely speculative at this time. Experiments are planned to address this point.

CONCLUSIONS

The microstructures resulting from three systems of HMX-based, plastic-bonded explosives pressed to various levels of porosity were studied. All three systems incorporated HMX prepared to the same particle specification. The first step in the consolidation process was elimination of large voids by deformation of the prills. Little fracture occurred in this step. Where it did occur, it was the result of large deformation of individual prills. This led to localized regions of high fracture density. As densification was further increased, fracture became more extensive until, at the highest densification, the majority of large HMX crystals exhibited extensive cracking. This cracking allows elimination of intragranular voids, which, evidently, is the last step in the densification process.

Using microscopy, the evolution of microstructure in PBX 9501 from a porosity of 21% to 0.6% was shown to follow this sequence.

1. Heterogeneous consolidation of molding powder prills by reducing interstitial space between prills with very little damage to large HMX crystals. Occasionally, individual molding powder prills were massively deformed. In these prills, significant fracture of HMX crystals occurred.

2. Increasing incidence of transgranular cracking and twinning in large HMX crystals as porosity was reduced to 1%.

3. Production of spall pullout artifacts, higher incidence of cracking associated with particle-to-particle contacts, and intercrystalline indentation/intergrowth migration for samples with porosities below 1%.

PBX 9404, which has different binder constituents, at 0.6% porosity exhibited microstructures very similar to those of PBX 9501.

The increased fraction of binder in X-0242 allowed densification to lower porosities than were achievable with PBX 9501. Even at 0.3% porosity, the increased fraction of binder in X-0242 was shown to significantly mitigate both phases 2 and 3 in this sequence above.

Attempts, using microscopy, to characterize void size distribution as a function of densification were unsuccessful. Experiments to do this using x-ray and neutron scattering and porosimetry techniques are underway.

While we have not yet been able to quantify our observations to our complete satisfaction, the trends observed can be plausibly related to the anomalous desensitization of very high density formulations of HMX. The apparent domain of easy prill boundary sliding is long past, as is that of coarse particle twinning. The major changes observed in the highest density samples arise from the coarse particles, not the fines and binder, and consist of their extensive comminution by the three-dimensional microcrack network, frequently associated with particle contact points or the introduction of spall pullout artifacts (which complicate porosity measurements), and of the intercrystalline indentation and intergrowth migration processes.

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