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Microstrain and Defect Analysis of CL-20 Crystals by Novel X-Ray Methods

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Microstrains and defects are introduced during synthesis and crystal-growth stages of energetic particles and increase during processing stages such as grinding, mixing, and extrusion. The detection and quantification of these microstrains and defects in a given particle population is a difficult task that requires highly sensitive techniques. In this study a novel X-ray diffraction technique (XAPS) based on simultaneous rocking-curve analysis of individual particles was successfully applied to CL-20 powders. The effects of synthesis, grinding, and static loads on the extent of microstrain and defect development in CL-20 particles were quantitatively determined as frequency versus half-width of rocking curves. The greater half-width values observed for the samples subjected to grinding and static loads indicated greater microstrain and defect density in comparison to the as-received samples of CL-20. It may be possible to relate the findings of such analysis to combustion calculations for energetic particles in general and to CL-20 particles in particular.

Keywords: CL-20, X-ray diffraction

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Introduction

CL-20 or hexanitrohexaazaisowurtzitane is a relatively new energetic material that exhibits higher density and heat of formation than RDX and HMX, the conventional energetic nitramines. These superior properties are due to its unique caged structure (isowertzitane) with characteristics of high density, strained ring, and high branching, respectively. Superior products already have been demonstrated by replacing the conventional nitramines with CL-20. These include solid rocket propellants, gun propellants, and shaped charge explosives.

The combustive properties of energetic materials such as CL-20 depend on their composition and microstructural characteristics such as molecular and crystal structure and particle size distribution [1]. Although some of these characteristics have been fairly well understood, the effects of more subtle features, such as molecular and crystal defects on the combustive properties of energetics, have not been investigated. The presence of microdefects such as misaligned domains and dislocations in single crystallites (particles) is known to increase their chemical activity, by straining the crystal lattice and making more reaction sites available at the domain boundaries and dislocation sites [2, 3]. The strain energy of a dislocation is about 8 eV for each atom plane threaded by the dislocation, while the core energy is in the order of 0.5 eV per atom plane [4]. This large positive stain energy means that the free energy of a crystal is increased by the introduction of a dislocation. Processing practices in crystal growth, such as solution stoichiometry, temperature, catalysts, impurities, and even mechanical vibrations, could induce defective and partially amorphous structures that would not be apparent to most conventional characterization techniques. Highly sensitive and reliable techniques are required to determine quantitatively the extent of these defects in energetics to optimize their processing parameters and energetic properties.

The goal of this project was to investigate the applicability of novel X-ray methods to quantitative determination of crystal imperfections, that is, microstrains and defects in CL-20 particles. For this purpose a very sensitive X-ray diffraction technique

(XAPS), which is based on the simultaneous rocking-curve analysis of individual particles [2,3,5,6] was applied to CL-20 powders.

Experimental Procedures

Materials

The materials used in this study were two CL-20 powder samples manufactured by Thiokol Corporation and provided by ONR. The two powder samples received had average grain size of 130 microns (coarse) and 6 microns (fine), respectively.

Some of the coarse (130 μm) CL-20 powder samples were subject to deformation under static loads to simulate processing conditions. The applied static loads ranged from 600 to 2000 psi and were held for 10 minutes. The deformation experiments were carried out at two temperatures of 25 and 90°C.

In addition to the as-received powders, new CL-20 crystals were also grown with different particle morphologies. These new crystals were grown and used, together with the as-received powders, for crystal structure analysis. All CL-20 samples were kept in sealed cups with neutralizing water suspension, except during testing. The sealed cups were placed in steel bomb enclosures during storage.

The Fourier transform infrared (FTIR) analysis of the powders was carried out, and the purity of the epsilon, ε, polymorph was established. The presence of the doublet between 8.20 cm^{-1} and 850 cm^{-1} (and the lack of a single peak) establishes the purity of the ε polymorph. ε-CL-20 is the most stable and energetically favorable polymorph.

The differential scanning calorimeter (DSC) scans of CL-20 powder were also carried out. The CL-20 crystals exhibit an exothermic transition (melting) at 168°C. The heat of fusion is 3.46 cal/g.

Characterization Methods: X-ray Analyzer for Particles (XAPS)

In this study the X-ray Analyzer for Particles (XAPS) method, which is based on simultaneous rocking-curve analysis

of individual particles, was employed to determine quantitatively the microstrain and defect distributions in CL-20 energetic crystals. XAPS is a suitable method for measuring the degree of imperfection and lattice misalignment of individual crystallite through X-ray rocking-curve half-width measurements [2,3,5,6].

Briefly, in the XAPS rocking-curve technique the powder sample is irradiated with a crystal monochromatized parallel X-ray beam (Figure 1). Each reflecting crystalline particle acts independently as the second crystal or test crystal of a double crystal diffractometer. Those particles, which are in reflecting positions, give rise to individual diffraction spots along the Debye arc (Figure 1). Each diffracting spot emanating from

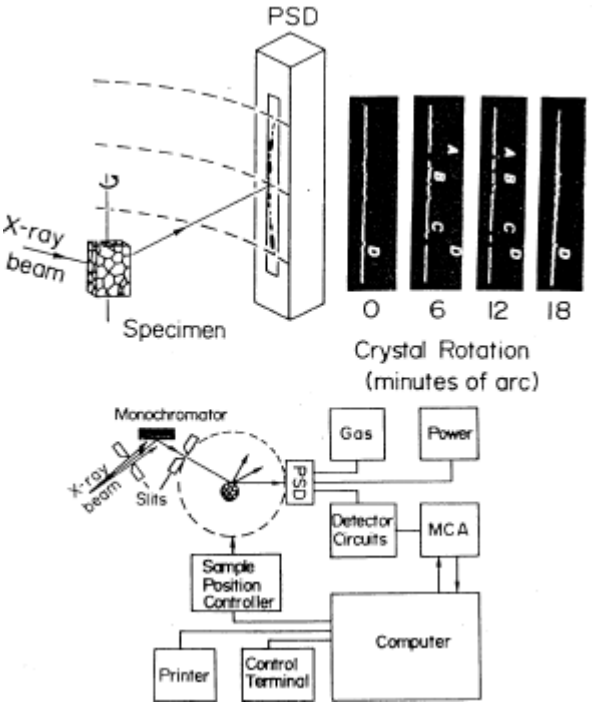

Figure 1. Principle of operation of XAPS particle rocking-curve analyzer.

the powder sample is registered as a function of location and intensity by a linear position-sensitive detector (PSD), which is aligned parallel to the Debye arc. After a short exposure the X-ray intensity spectra are collected by a multichannel analyzer (MCA) and stored by a computer (Figure 1). When the data transmission is completed, the sample is rotated automatically by a chosen increment (1 minute of arc) before the next exposure is started. This stepwise rocking process is repeated until the entire angular range of the grain reflections are recorded (20 minutes of arc). The rocking curve for each particle as well as the rocking curves for the entire particle population are computed by analyzing the entire reflection matrix. The rocking-curve half-width (full width at half maximum intensity) provides a measure of microstrain and angular lattice misalignment induced by dislocations within the diffracting grain (Figure 2).

The width at half the maximum intensity of the rocking curve (half-width) or (β) provides a measure of the angular lattice misalignment of the crystallite. Thus, the half-width (β) values provide information about the local densities of the accumulated excess dislocations of one sign, that is, or same orientation, with respect to lattice directions.

Some illustrations of the relationships between the distribution of excess dislocations and the resultant rocking-curve profiles are schematically shown in Figure 2. If the profile is smooth, a homogeneous distribution of excess dislocations would, as marked in ''deformed'', exist. If, on the other hand, a multipeaked profile is produced, the excess dislocations are heterogeneously distributed, giving rise to distinct lattice tilts as would be encountered, for example, in grains with subgrain boundaries, as marked ''polygonized.'' The angle between the subpeaks of such rocking curves then would represent the relative misorientation of adjacent lattice domains or subgrains, whereas the width of well-resolved subpeaks indicate the degree of internal distortion in these domains. Annealed grains with low excess dislocation densities give rise to smooth rocking curves with small β values as marked in ''annealed.''

Assuming that the excess dislocations are randomly located in the grains and thus can be represented by a Gaussian

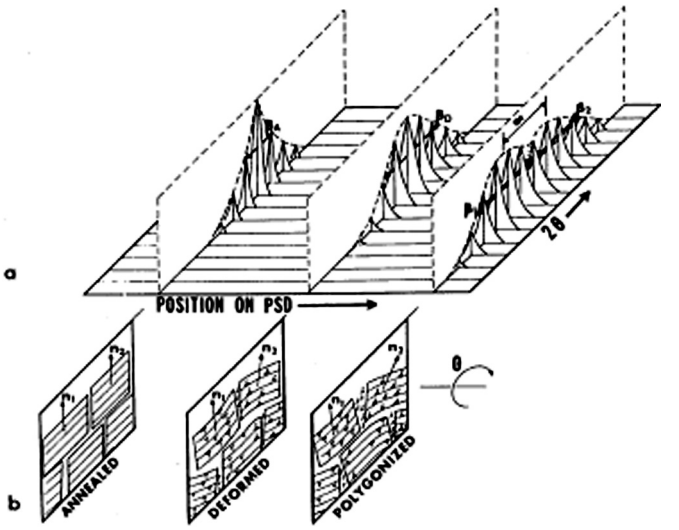

Figure 2. Rocking-curve and particle defect structure characteristics (schematic). (a) Construction of rocking curves. (b) State of the related particle defect structures.

distribution, the excess dislocation density is determined by $D=\beta^2/9b^2$, where b is the magnitude of the Burgers vector. If the excess dislocations are aligned in the subgrain boundary and the tilt angle of adjacent subgrains, ε', is measured, the excess dislocation density in the subgrain boundary $D_{SB} = \varepsilon'/3bt$, where t is the subgrain size [7]. If resolvable, the subgrain size can be measured from the images of X-ray reflection topographs.

The microstrains, that is, the residual strains (and stresses) in individual crystallites or particles, induced by the excess dislocations can also be calculated from the excess dislocation density D values, provided that the exact natures and distributions of the excess dislocations are known and the crystal structure and physical constants are available. The microstresses associated with a dislocation are biaxial in nature and vary inversely with distance from the dislocation core. Although the stresses at the core reach to infinite values, more reasonable stresses are induced over the average body of the crystal [4].

A Picker four-circle goniometer was utilized for XAPS experiments. CuK_α radiation monochromatized with a Si (111) crystal at 35 kV and 20 mA was used. Five to 15 minutes timed exposures were applied at each rocking step. Three hundred to 1000 individual particles were evaluated from each sample.

Other Methods

Wide-Angle X-ray Diffractometry. Wide-Angle X-ray Diffractometry (WA-XRD) was utilized for determination of the degree of crystallinity of the CL-20 powders. Computer-aided deconvolution methods with Images software were applied to determine the relative contributions of the amorphous and crystalline portions of the samples from their diffraction patterns. The unit used was the Rigaku DXR-3000 diffractometer system. CuK_α radiation at 40 kV and 20 mA and a graphite monochromation with focusing geometry were used for all WA-XRD runs.

Kappa Diffractometry. Kappa diffractometry was used to carry out single-crystal analysis and to determine the crystal structure parameters. This work was carried out because the crystal structure parameters were required for dislocation density calculations. A Nonius Difractis 586 X-ray unit and CAD4 and NRC software packages were used for single-crystal analysis.

Scanning Electron Microscopy. A scanning electron microscope (SEM) was used to examine the particle morphology. A JEOL 840 SEM with EDX was utilized for this purpose.

Results

Crystal Structure Analysis

The crystal structure of ε-CL-20 was determined using one of the crystals grown from solution. The results of these preliminary studies indicated the following:

Crystal system	Monoclinic
Unit cell parameters:	$a = 8.84$ (2) Å
	$b = 12.50$ Å
	$c = 13.36$ Å
	$\alpha = \gamma = 90^\circ$
	$\beta = 106.8^\circ$
Unit cell volume:	$V = 1414.3$ Å^3
Number of molecules per unit cell:	$z = 4$
X-ray density:	$d = 2.04$ g/cc

from $d = zM_w/(VN_A)$ with molecular weight equal to 438.24.

XAPS Curves

Typical XAPS rocking-curve data, that is, intensity versus position versus rotation, as stored in the computer memory is shown in Figure 3. The data shown are only a small portion of a single rocking-curve run, where 2/3rd of the rotations and 2/3rd of the channels were omitted for simplification. The analysis program locates the intensity from a specific particle at a specific MCA channel(s) at a specific rotation step and follows its variation at the same channel(s) in each rotation and obtains the rocking-curve distributing profile before calculating the width at half maximum. This procedure is carried out for each reflecting grain. Twenty to 100 grains are analyzed in each run.

Coarse versus Fine (Ground) CL-20 Powders

The results of the XAPS rocking-curve analysis of the as-received coarse (Figure 4) and fine CL-20 powder samples are shown in Figures 5 and 6, respectively. In these figures the statistical distribution of the half-width values of the individual particles is exhibited as the particle frequency observed for each half-width value. In these graphs the larger half-width values emanate from those particles, which constitute high microstrains and defects, and, conversely, the smaller half-width values emanate from those particles, which exhibit a

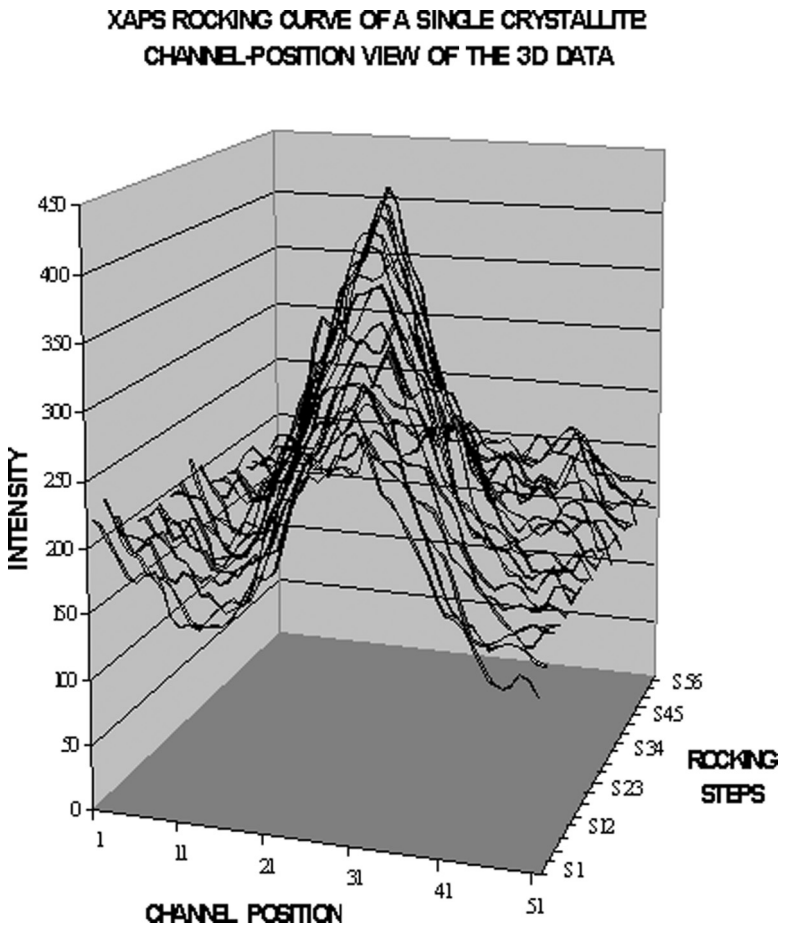

Figure 3. Rocking-curve step scan patterns.

smaller number of defects and low microstrains. The rocking-curve half-width mean values of the fine powder (5.1 minutes of arc) were measurably larger than that of the coarse powder (4.2 minutes). Also, the maximum half-width value observed in the fine powder (38 minutes) was considerably higher than the coarse powder (18 minutes).

Assuming that the excess dislocations are randomly located in the grains, the excess dislocation density $D = \beta^2/9b^2$ can be

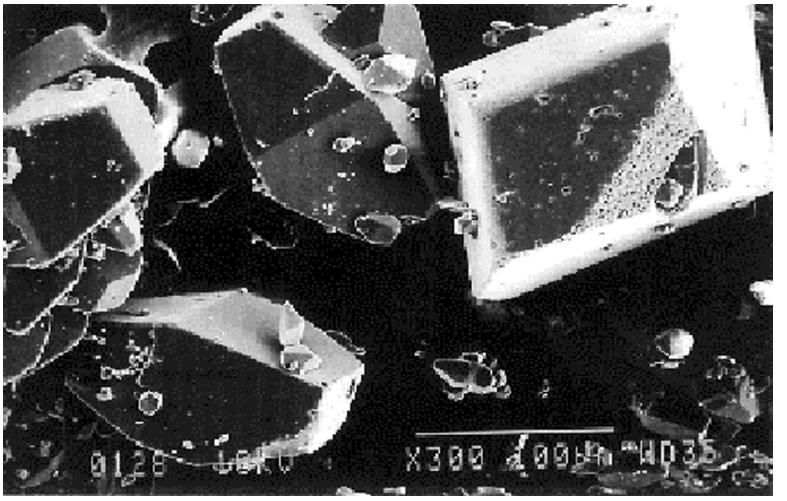

Figure 4. As-received coarse CL-20 powder at 300 × magnification.

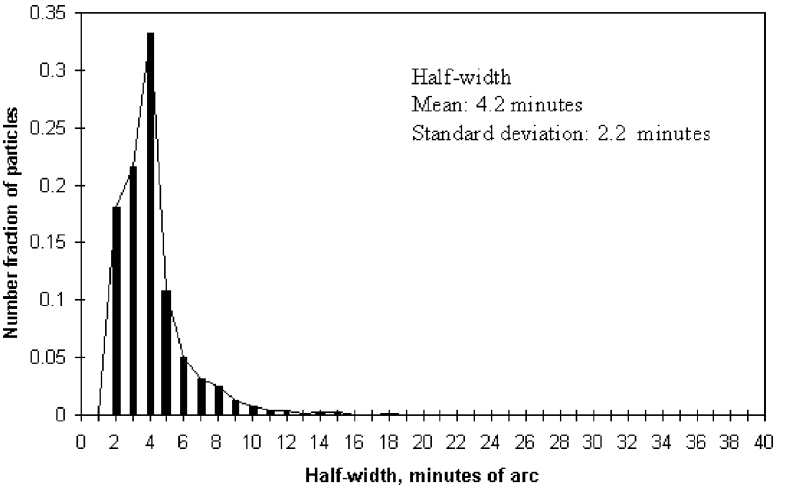

Figure 5. Particle defect half-width distribution by XAPS for as-received coarse CL-20.

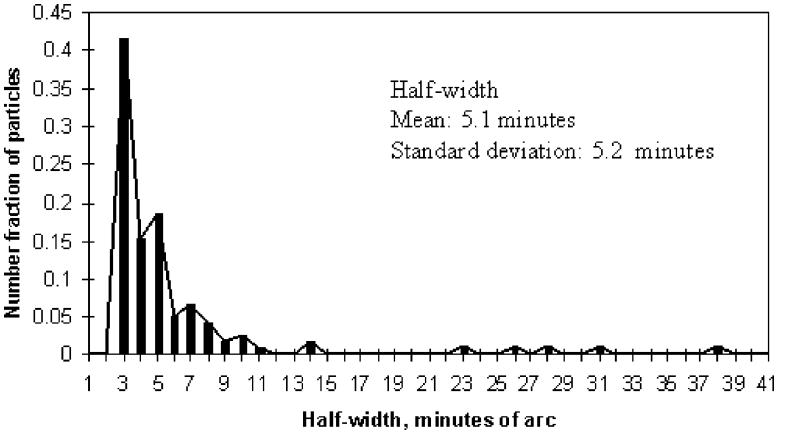

Figure 6. Particle defect half-width distribution by XAPS for as-received fine CL-20.

calculated for each case. Taking the Burgers vector $b = 8.84\text{Å}$, then the excess dislocation density values can be determined. For the as-received coarse powder the excess dislocation density is $2.1 \times 10^7/\text{cm}^2$, and for the as-received fine (ground) powder it is $3.1 \times 10^7/\text{cm}^2$.

A fine CL-20 batch was obtained by grinding of the as-grown particles. The higher half-width values of the fine CL-20 powder, therefore, could be taken as a measure of the effect of the grinding process on the crystal defects. Thus, the applied grinding process appears to have increased the lattice imperfections and defects in the CL-20 particles. The XAPS rocking-curve technique, therefore, can be utilized to determine quantitatively the effects of grinding on crystal defects.

The typical results of the WA-XRD scans are shown in Figures 7 and 8 for the coarse and fine powders, respectively. According to the deconvolution analysis carried out on these patterns, the degree of crystallinity of the CL-20 powders was in the range of 90–93%. The difference in the degree of crystallinity of the coarse and fine powders was negligible.

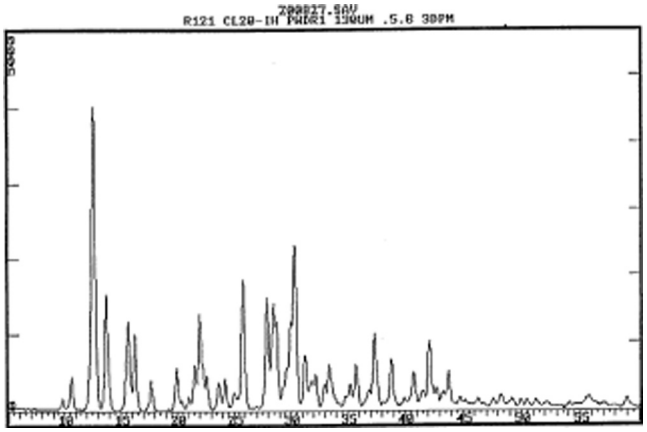

Figure 7. Wide-angle X-ray diffraction pattern of coarse CL-20 powder.

CL-20 Powders Subjected to Deformation

As noted earlier, specimens of the coarse CL-20 powder were subjected further to uniaxial compression (Figure 9), using a modified compression-molding machine to simulate the

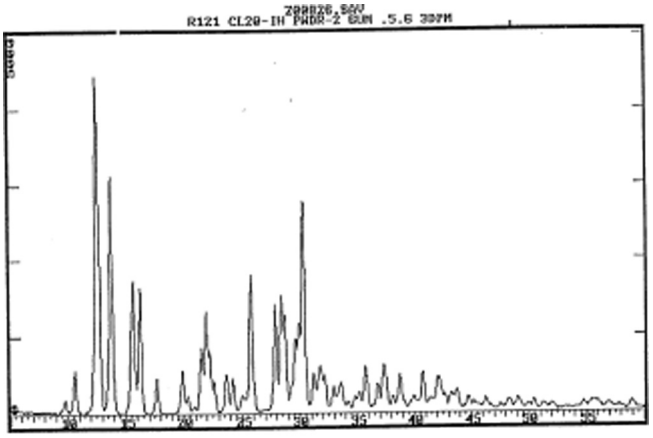

Figure 8. Wide-angle X-ray diffraction pattern of fine CL-20 powder.

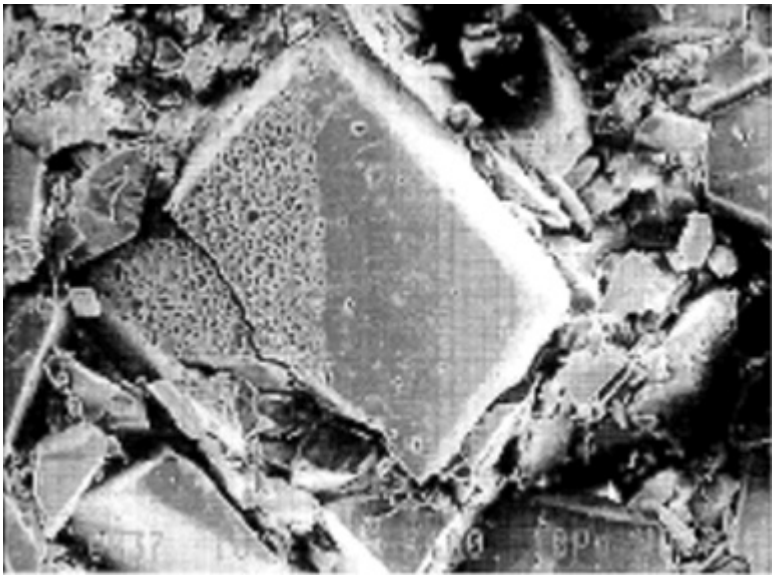

Figure 9. Coarse CL-20 particles fractured under static load.

thermomechanical conditions that they would experience during further processing. During these processes high shear stresses are generated, and the particles generally undergo shear deformations. Invariably, it is the excess shear stresses that cause the microplastic deformations in the crystals. Under adequately high shear stresses, crystals tend to generate dislocations along their slip-planes and shear deform by slip. The ''characteristic slip-plane'' of a crystal tends to be the lattice plane where the separation between the atoms/molecules is maximum.

By applying normal loads to randomly oriented crystallite particles, ''resolved shear stresses'' are generated along the ''characteristic slip-plane'' of each particle. The magnitude of the shear stress would vary depending on the orientation angle of the characteristic slip-plane and the characteristic slip direction of the given particle with respect to the direction of the applied normal stress. For the angle between the applied normal stress direction and the characteristic slip-plane normal being ϕ, and the angle between the slip direction and

the slip-plane normal being λ, the relationship between the applied normal stress σ_{app} and the resolved shear stress τ_{rss} (on the characteristic slip system of a single crystal) is given by [4]

$$\tau_{rss} = \sigma_{app} \cos\phi \cos\lambda.$$

This shear stress resolved on the characteristic slip-plane and in the slip direction of a single crystal ranges from zero, for either $\phi = 0$ to $\lambda = 0$, to maximum, for $\phi = \lambda = 45°$. The maximum resolved shear stress is

$$\tau_{rss(max)} = \frac{1}{2}\sigma_{app}.$$

Therefore, in the static-load experiments carried out in this work, the effective or resolved shear stresses (τ_{rss}) on individual particle slip systems ranged from 0 to 1,000 psi for the $\sigma_{app} = 2,000$ psi experiment.

The typical results of the XAPS rocking-curve analysis of the coarse CL-20 powder (subjected to deformation under a static load of 2000 psi for 10 minutes time at 90°C) are shown in Figure 10. The mean half-width value exhibited by the CL-20 crystals increased upon being subjected to pressure (the increase was from 4.2 minutes of arc of the as-received coarse CL-20 particles to 9.4 minutes of arc upon pressurization). Upon pressurization the breadth of the half-width values increased substantially with the maximum half-width value reaching 40 minutes of arc upon pressurization. The mean excess dislocation density upon pressurization became $1.1 \times 10^8/\text{cm}^2$, with a maximum value of $1.9 \times 10^9/\text{cm}^2$.

The significant increase in the mean half-width value upon pressurization primarily arises from the generation of a relatively small number of particles (about 5% by number), which exhibit half-width values in the 20–40 minutes range. If these relatively few particles that exhibit such high half-width values are removed from the analysis, the magnitude of the half-width difference between the particles subjected to the 2000 psi load versus those that were not reduces considerably.

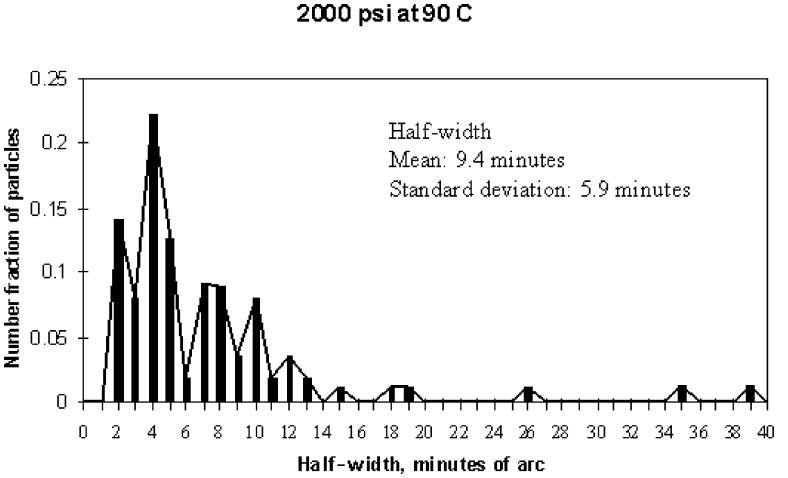

Figure 10. Particle defect half-width distribution by XAPS for CL-20 subjected to 2000 psi.

The mean half-width of the CL-20 particles subjected to pressurization becomes 6.44 when the particles with half-width values in the 20–40 range are not included in the analysis. Thus, upon axial compression and the associated deformation the increase in the defect density of the CL-20 powder is associated with the introduction of microstrains and defects to a relatively small number of particles, which presumably carry the load during axial compression of the powder bed.

Conclusions

The applicability of the novel X-ray method XAPS to the quantitative determination of crystal defects and excess dislocation density of the CL-20 crystals has been demonstrated.

Acknowledgments

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