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X-ray microdiffraction studies of mesoscale structure and dynamics below the size of most polycrystalline grains

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Advances in x-ray microdiffraction make it possible to non-destructively measure crystallographic distributions at a spatial resolution below the size of most polycrystalline grains. This fundamentally new information allows unprecedented studies of how stress, crystallographic orientation and grain morphology interact to affect the dynamics of mesoscale structure. We describe recent high-precision experiments with submicron x-ray beams that map two *and* three dimensional grain orientation and strain *tensor* distributions to ~ 1 part in 10^4. These examples illustrate how this new class of measurements can be used to study mesoscale structure and dynamics to address long-standing issues in materials science.

Introduction

The behavior of materials is inherently dependent on three-dimensional tensor distributions. Heterogeneous networks of second phases, misoriented grains, voids, reinforcing particles and fibers act to redistribute macroscopic applied loads into complex, three-dimensional distributions of stresses and strains. Even fundamental properties such as length scales, phase transitions, slip behavior, and chemical order change drastically between two-and three- dimensional systems. Yet despite the importance of three-dimensional structure in materials behavior, measurements are dominated by one- and two-dimensional analytic techniques.

The availability of high brilliance x-ray sources and new developments in x-ray optics now makes it possible to produce high-intensity penetrating submicron x-ray beams. Monochromatic microbeams below 0.1 μm-D have been demonstrated and polychromatic beams as small as 0.7 μm-D are now available. Such beams allow for high resolution (submicron) mapping of phase, texture and strain at a length scale which is smaller than the typical grain size in most polycrystalline materials. This fundamentally new information is essential to understand materials behavior at the mesoscopic scale of 0.1-10 μm; stress is a major driving force in mesoscale structural evolution and materials behavior. Not only two-dimensional but also three-dimensional crystallographic information can be recovered and with unprecedented sensitivity to strain and lattice rotations.

X-ray microdiffraction on polycrystalline materials is especially challenging and requires specialized instrumentation and techniques; for a single grain, the probability of a Bragg reflection is vanishingly small with a monochromatic beam and an unknown crystal orientation. Whereas small single crystals can be bathed in large x-ray beams and studied with standard diffraction-rotation methods, polycrystalline microdiffraction patterns are complicated by sphere-of-confusion motions and by changing grain illumination as the sample is rotated (Fig. 1). The complexity introduced by sample rotation can be avoided by the use of broad-bandpass Laue methods.

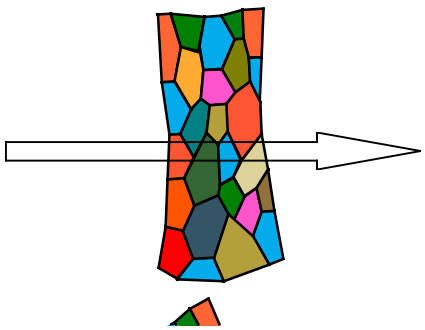


Fig. 1 A small penetrating x-ray beam intercepts various grains in a polycrystalline sample which change as the sample is rotated. Different grains are illuminated because (a) the penetrating beam has a high depth to transverse cross-section ratio, which in polycrystalline samples makes it impossible to ensure that the same grains are illuminated as the sample is rotated, and (b) because the sphere of confusion for state-of-the-art diffractometers is greater than 1μm[3].

White-beam Laue diffraction is a standard crystallographic method widely used to determine crystal orientation without rotation of the sample.[3,4] A "white" or broad-bandpass beam is directed onto a sample and wavelengths which satisfy the Bragg condition with planes in the crystallites are reflected. (Fig. 2). With suitable instrumentation, the Laue method can be used to precisely determine the orientation (local texture) of individual grains and their deviatoric (distortional) strain. Laue diffraction can be further extended by measuring the energy of one or more reflections to determine the full strain tensor in polycrystalline samples. In order to measure strain *distributions*, a large number of measurements must be collected. This requires automated methods such as described previously.[5,6]

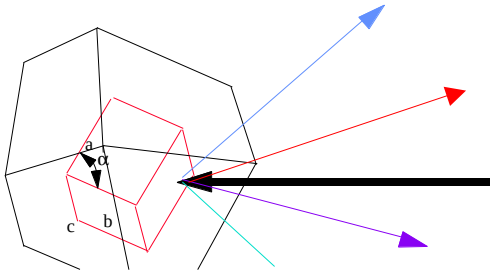
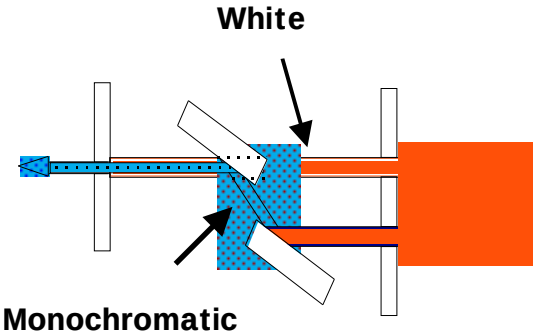


Fig. 2 The unit cell shape can be determined from 4 independent Bragg reflections. The volume of the unit cell is determined by measuring the d spacing of one reflection. (one energy measurement).



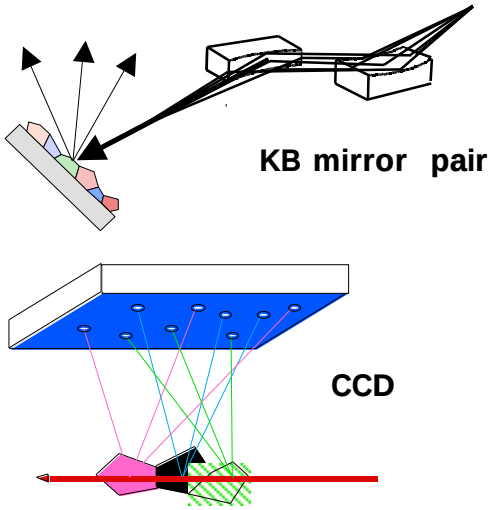


Fig. 3. The three essential elements for x-ray microdiffraction on a polycrystalline sample: (top) a microbeam monochromator for accurately measuring the x-ray energy; (b) nondispersive focusing optics and (c) a high accuracy x-ray area detector.

The experimental steps required for microdiffration measurements of strain in polycrystalline samples are illustrated in Fig. 3. A broad-bandpass microbeam intercepts a sample and illuminates a small number of crystal grains. The overlapping Laue patterns from the grains are recorded on an area detector and fit to find the intercept of each reflection. The pattern is then indexed to determine the indices of each reflection and the number of reflecting grains. The texture (orientation) and relative or absolute strain tensors are determined for the illuminated grains. The absolute d-spacings can be calibrated by inserting a scanning monochromator into the incident beam in such a way that the focused beam spot does not move at the sample.

Although there may be many overlapping Laue patterns, each one is a complete single-crystal pattern. Single crystal diffraction directly measures the average local strain tensor of a grain through the orientation of the unit cell and the distortion of the lattice parameters from their (unstrained) values. Chung and Ice[6] have described how the deviatoric strain tensor can be recovered from the precision measurement of four Bragg reflections where no three reflections are in the same plane. The key steps in the process are the calibration of the instrument, the identification of the Bragg spot positions, and the automatic indexing of the reflections. The dilitational strain tensor can be determined if the energy of one reflection is determined.

With undulator sources, care is needed to optimize the instrumentation for both broad-bandpass and monochromatic operations. The bandpass onto the sample and the solid angle subtended by the detector determine the number of diffraction spots detected with Laue diffraction. For simple FCC metals, the reciprocal space volume per reflection is about $\frac{1}{2}\frac{1}{(3.5)^3} = 0.012$ Å^{-3}. In a geometry where an area detector at 90° to the beam is used to collect the diffraction spots, the volume of reciprocal space collected is given by $\frac{d\lambda}{\lambda}\frac{1}{\lambda^3}\frac{A}{R^2}$ as shown in Fig. 4. Here A/R^2 is the solid angle subtended by the detector, λ is the x-ray wavelength, and $d\lambda/\lambda$ is the bandpass of the x-ray beam. The number of reflections which can be collected for a typical FCC metal is therefore given by,

$$N \cong 85\frac{d\lambda}{\lambda}\frac{1}{\lambda^3}\frac{A}{R^2} \quad . \qquad (2)$$

In typical experiments, a solid angle of about 0.25-1 steradians can be collected; $A/R^2<1$. Therefore at 20 keV at most 10 reflections will be collected with a 3% bandpass. We note that at 10 keV a 20% bandpass will collect at most 8 reflections and from 6-10 keV only about 10 reflections can be intercepted.

Bandpass and x-ray energy can therefore be adjusted to optimize the experimental conditions. Too few reflections and it is difficult to index the pattern. Too many reflections and it is difficult to index overlapping patterns from multiple grains. High energy reflections (high indices) have narrower Darwin widths. Low energy reflections have greater integrated reflectivity. In addition, angular accuracy is improved with greater distance to the detector for a given pixel size (decreased solid angle subtended).

Undulator and monochromator

The bandpass of an undulator can be controlled by tapering the undulator or by collecting off-axis radiation. For cases where the highest brilliance monochromatic radiation is needed part of the time, it is convenient to tailor the beam bandpass by collecting on or off axis. Type A undulators at the Advanced Photon Source (APS) have narrow ~1% bandpasses on axis. Off-axis the spectrum is red shifted and broaded.. This ability to control the incident beam spectrum has been used in the design of the

microbeam monochromator to tailor the spectrum for highest brilliance when in monochromatic mode and for increased bandpass when used in "white-beam" mode. The spectra from a type A undulator on axis and vertically off axis by 1 mm is shown in Fig. 5. The monochromator uses a very simple water cooled design because the total power onto the crystals is low (small emittance accepted) and causes negligible distortion.[6,7]

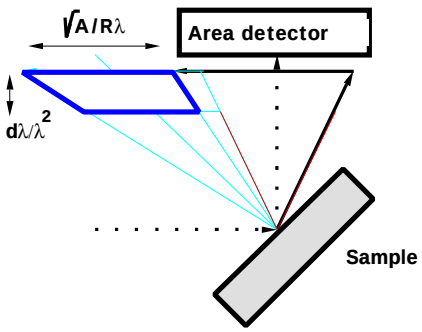


Fig. 4. Reciprocal space volume measured is determined by the solid angle of the area detector and the energy bandpass.

KB mirrors

The microprobe uses specially fabricated Kirkpatrick-Baez mirrors to produce submicron x-ray beams. The mirrors are produced by differentially coating spherical mirrors. With ideal mirror surfaces it should be possible to achieve beams as small as 0.25 µm-D with the current geometry. The mirror fabrication and performance is reported elsewhere.[8]

CCD Detector

The detector currently used for the x-ray microbeam experiments is a commercially available Princeton Research 1 megapixel CCD detector with ~22 µm pitch. This detector uses a CsI phosphor bonded to a 1:1 glass taper for radiation protection of the CCD chip and for efficient transfer of the visible radiation to the chip. The CCD

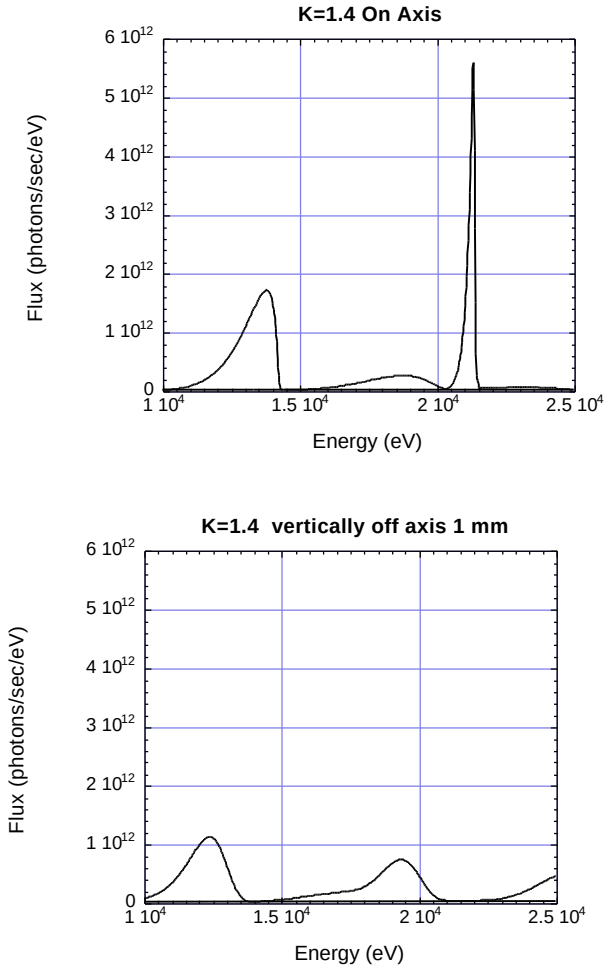


Fig. 5 Flux through a small pinhole (top) on axis and (bottom) 1 mm above the axis of a type A undulator at the APS.

linearity was calibrated by mounting it to a precision xy stage and surveying the nonlinearity of the pixel positions. Negligible systematic errors were detected at the level of 1 part in 10^4. However the detector response must be corrected for parallax and for variable efficiency of individual pixels; difference in efficiency can cause subpixel peak shifts that are significant for precision measurements of strain. The detector orientation with respect to the incident beam and sample is calibrated by measuring the peak positions of an unstrained monolithic single crystal (e.g. Ge or Cu).

First measurements with the x-ray microdiffraction station

The ability to measure submicron crystal structure below the surface region of a sample, opens up a number of interesting experimental possibilities. By observing true three-dimensional structure in-situ there is an opportunity to gain insights into such diverse fields as grain growth, crack propagation, deformation and creep. X-ray microdiffraction studies are particularly valuable for understanding the key mechanisms that control the growth and behavior of modern highly engineered materials that contain multiple layers. In many thin film materials for example, the character of the layers can be strongly influenced by either the underlying substrate or by thin-film overlayers. The three brief examples presented below illustrate the power of microdiffraction to study the influence of a substrate on an overlayer, the influence of cap and substrate on a buried thin film, and the developing structure in a complex three-dimensional process.

High T_c superconductor grain texture and growth mechanisms

Although single superconductor crystals can have very high critical currents, polycrystalline superconductors have limited critical current arising from the weak-ling behavior of high-angle grain boundaries. Recent work at the Oak Ridge National Laboratory has found that the current carrying capacity of highly-textured high-T_c polycrystalline films can be greatly increased by a process called roll-assisted-biaxial-textured-substrates (RABiTS). The details of the grain growth mechanisms are however critical to improving the current carrying performance of the films. Budai et al.[9,10] have recently reported measurements of the three-dimensional structure of real RABiTS samples which show how each high T_c grain is effected by the underlying Ni grain and the intermediate grain layers. The orientation of each high T_C superconductor grain is measured with high accuracy simultaneously with the orientation of the buffer and nickel substrate grains directly below it. This information is only possible with a penetrating high-resolution probe. Measurements can be made on a large number of grains to develop good statistical understanding of the mechanisms affecting the superconductor texture. The results of the measurements show systematic tilting and grain growth mechanisms with far greater precision than with any previous study and lend new understanding into how to control the final superconductor film texture.

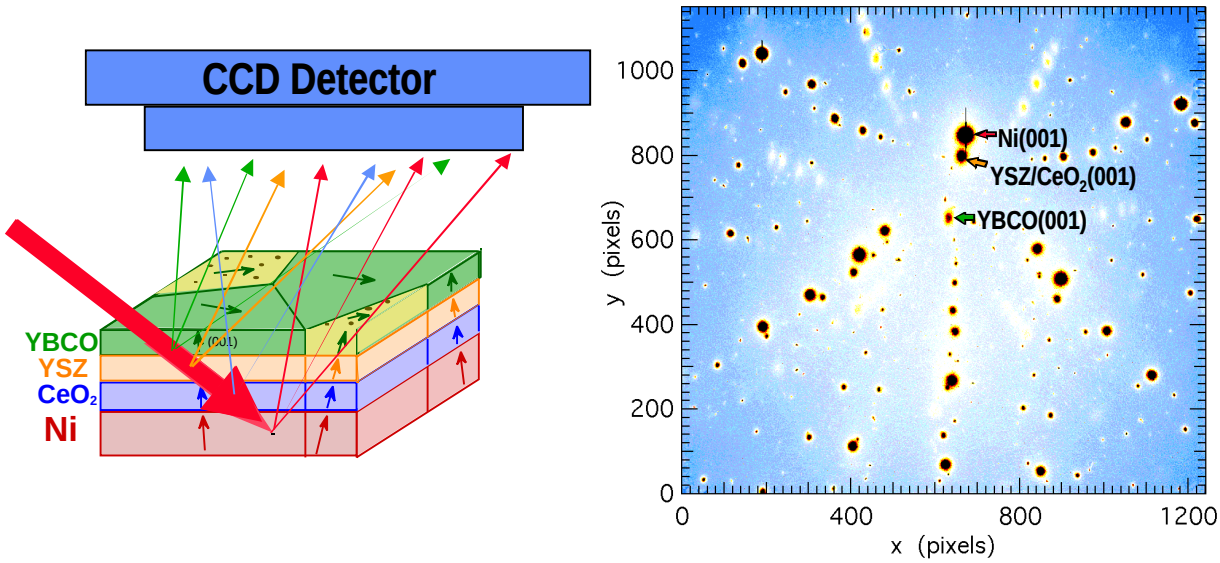


Fig. 6 The penetrating ~20 keV x-ray beam generates a Laue pattern for each grain in the layers of the RABiTS structure. As shown in the image, there is a tendency for the 001 orientation of each layer to move toward the surface normal. This behavior has been measured with high precision and interpreted in terms of geometrical growth of films with mismatched unit cell parameters.[9,10]

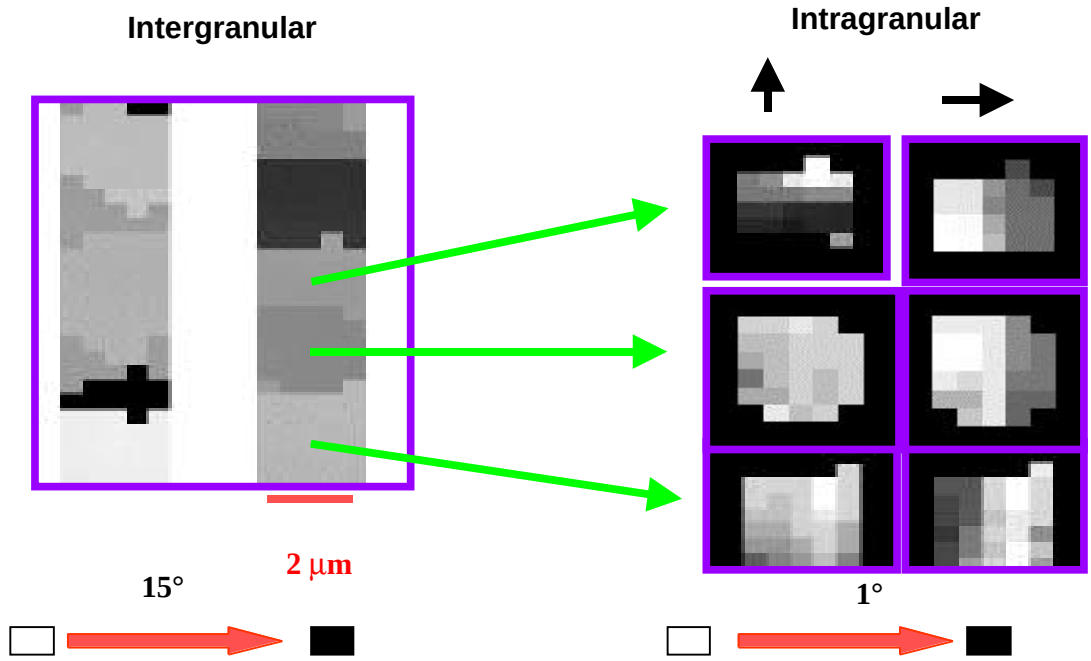


Figure 7. Bamboo structure of the high-angle grain boundaries of grains in an aluminum interconnect are easy to see (15 ° range) while at the subgrain level, the structure shows a more complicated orientation distribution within each grain (1° range). The intra-granular structure of the grains is dominated by lattice rotations, while the inter-granular structure exhibits large strain variations.

Interconnect strain tensor and subgrain rotations The failure of electronic interconnects in integrated circuits is long-standing issue of concern as IC feature-sizes shrinks. Stress, crystalline heterogeneities, and interconnect morphology are known to contribute to interconnect failure and it has long been a goal to monitor interconnect stress distributions and grain orientation/morphology in real time. Recent measurements by Yamomoto and Sakata[10]., Solak et al.,[11] Cargill et al.,[12]Tamura et al.[13]and others have demonstrated the application of x-ray microdiffraction to study crystal prooperties related to reliability of interconnects. A major advantage of *microdiffraction Laue* measurements is the ability to determine the full strain tensor at a grain-by-grain (inter-granular) or subgrain (intra-granular) level. Tamura et al.[14]and Chung et al.[15] have recently reported pioneering measurements of subgrain rotations and strain tensors in electronic interconnects. For example, as shown in Fig. 7, the orientation of grains in a thin Al interconnect wire can now be mapped with 1 part in 10^4 resolution. In the interconnects studied, the grains are composed of ~1-2 μm grains with large angle grain boundries and subgrains with much lower angle grain boundries (Fig. 7).

Deformed materials

Initial measurements on deformed Al crystals demonstrate the full power of x-ray microdiffraction to characterize three dimensional processes and structure. In these measurements, the x-ray beam intercepted an Al sample near a triple grain junction. The diffraction pattern was collected at 10 different distances from the sample by translating the detector with a precision vertical stage (0.1µm resolution). Although the data analysis is still underway, the images are rich with details about the deformation process. Single grains deform into subgrains that rotate with respect to each other. These rotations and the strain in the subgrains can be quantitatively determined. In addition, by triangulation, the position of each subgrain can be calculated. The subgrain structure from one of the ~20 reflections collected is shown in Fig. 8 at two different distances from the sample. The ray tracing required to determine the subgrain location is indicated schematically. The sensitivity to subgrain location along the incident beam is under investigation, but resolution of a few microns or less should be possible. This unprecedented sensitivity to crystallography in three dimensions opens up a whole new branch of materials studies.

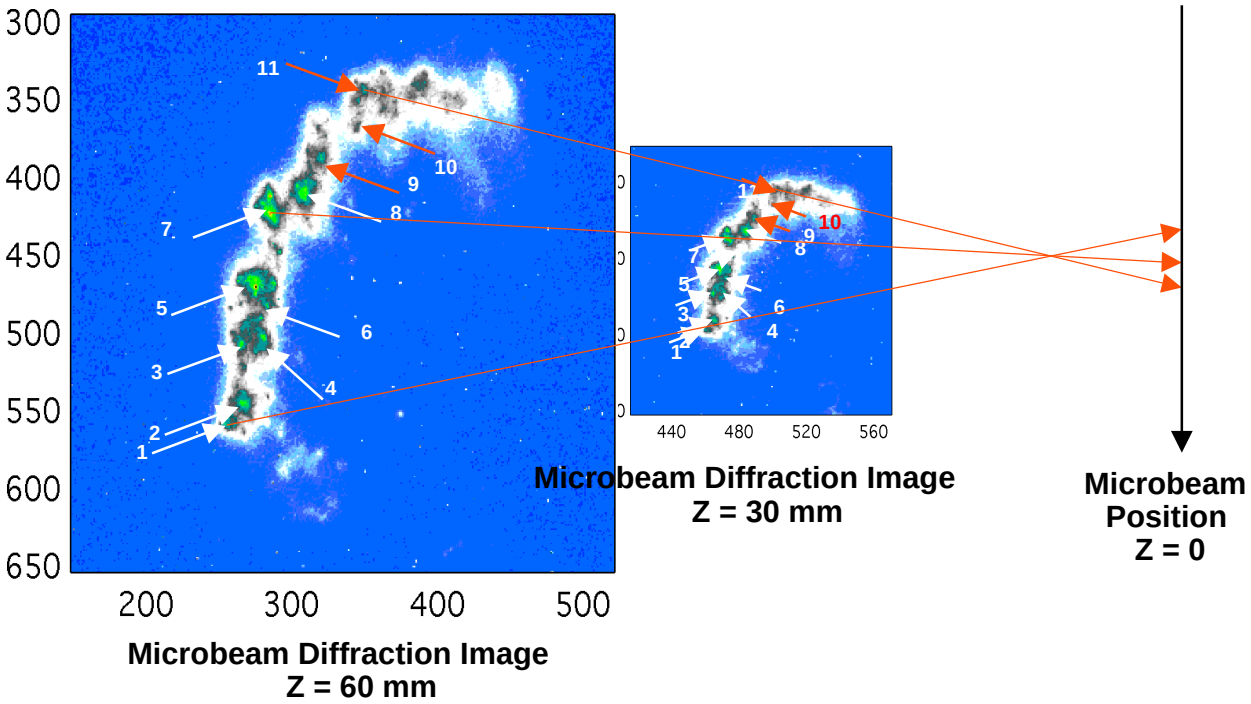


Fig. 8. X-ray microdiffraction measurement of a deformed Al grain. The grain has broken into subgrains with small angle grain boundaries.

Conclusion

Intense x-ray synchrotron sources and new x-ray optics now make it possible to study the mesoscale structure of materials in three dimensions. For polycrystalline materials, wide-bandpass techniques are essential and can provide submicron spatial resolution and subcubic micron volume resolution. Early experiments with an advanced x-ray microdiffraction station illustrate how x-ray microdifraction can provide new information on the structure, growth and dynamics of advanced materials.

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