X-Ray Diffraction Signatures of Defects in Nanocrystalline Materials


Center for Materials Research and Analysis
University of Nebraska-Lincoln
Lincoln, Nebraska 68588

Abstract

A computational technique is presented to calculate x-ray diffraction patterns from nanocrystalline materials containing defects. Stacking and twin faults were introduced into spherical and cubic shaped face-centered cubic nanocrystals. The calculated diffraction patterns from the faulted nanocrystals display peak shifts and peak broadening consistent with current theories concerning the effects of stacking faults on x-ray diffraction powder patterns. In addition, it was determined that stacking fault location in the crystallite has a great effect on the magnitude of the peak shifts. Analysis was also performed for the addition of up to 20 percent point defects in the nanocrystalline model and these effects on the x-ray diffraction patterns were studied.

Introduction

The intensity scattered from an array of atoms can be expressed by the Debye scattering equation:

\[ I = \sum \sum f_m f_n \frac{\sin(kr_{mn})}{kr_{mn}} \quad \text{Eq. (1)} \]

where \( k = \frac{4\pi \sin \theta \lambda }{ \lambda } \), \( r_{mn} \) is the interatomic distance, and \( f_m f_n \) is the product of the atomic scattering factors for the \( m \) th and the \( n \) th atoms. This equation yields the intensity distribution from a powder pattern made up of randomly oriented nanocrystallites.

Previous work with calculated patterns from nanocrystals involved simulations of grain boundaries, mixed atom types, powder diffraction, and uniform strain. This work investigates the effects on the powder diffraction patterns of three types of crystal defects in face-centered cubic (FCC) structure.

Models

Face-centered cubic models were created by defining the \( x, y, z \) coordinates of each atom. Two shapes of crystals were employed in these calculations, cubic and spherical. Both models were created by stacking (111) planes resulting in a 10 by 10 by 10 unit cell cube and a 12 unit cell diameter sphere respectively. Three types of defects: 1) vacancies, 2) stacking faults, and 3) twin faults were introduced into these models. Vacancy concentrations of 0, 4, 10, 15, and 20 percent...
were introduced by randomly removing atoms from the model until the desired concentration was obtained. Next, models with a stacking fault (example: ABCABCBCABCABC) were created. This was achieved by altering the stacking sequence of each (111) plane as the models were created. Finally, models containing a twin fault within the (111) stacking (example: ABCABCBCABCABCA) were created.

A Fortran computer program was written to calculate all the distances \( r_{mn} \) in the model. The intensity in terms of \( k\alpha \), where \( \alpha \) is the lattice parameter, was then calculated using the Debye scattering equation (Eq. 1). The resulting intensity was normalized by the number of atoms in each model and is reported as \( I(\text{eu})/(N^*f) \) where \( N \) is the number of atoms in the model and \( f \) is the atomic scattering factor.

Warren reports equations that relate the effects of stacking faults on powder patterns of FCC crystals. The shifts in the (111) and (200) peaks are a function of the stacking fault probability, \( \alpha \), and are related by:

\[
\Delta (2\theta)^{\circ}_{(111)} = \frac{90\sqrt{3} \alpha \tan \theta_{111}}{\pi^2} (1/4) \quad \text{Eq. (2)}
\]

\[
\Delta (2\theta)^{\circ}_{(200)} = -\frac{90\sqrt{3} \alpha \tan \theta_{200}}{\pi^2} (1/2) \quad \text{Eq. (3)}
\]

As a result of stacking faults, these equations predict that the (111) peak will shift to a higher angle and the (200) towards a lower angle with the (200) shifting twice as far as the (111).

**Results and Discussion**

**Vacancies**

Effects of vacancy concentrations on the calculated (111) and (200) diffraction peaks are shown in Figure 1a. Using \( k = 4\pi sin\theta/\lambda \), and the lattice parameter of a copper crystal, the corresponding 2\( \theta \) angles are listed at the top of Figures 1a and 1b. was made using copper K\( \alpha \) radiation. The intensities of the diffraction peaks decrease with increasing vacancy concentration. As expected, the background intensities increase with higher vacancy concentration which is shown in Figure 1b. This increase in background intensity is related to the concentration of vacancies as predicted by the Laue formula:

\[
I = C\lambda C_v (f_A-f_v) \quad \text{Eq. (4)}
\]

where \( C \) and \( f \) are the concentrations and atomic scattering factors of the atoms (A) and vacancies (V). The scattering factor of the vacancies is zero. Plotting the background intensity at a fixed value of \( k\alpha \) of 15 versus the Laue formula results in a very good correlation between the two as shown in Figure 2.
To create models with different amounts of stacking fault probability, $\alpha$, a stacking fault was placed at different locations from the center ($\alpha$ is maximum) to near the edge of the spherical model ($\alpha$ is minimum). In these spherical models, $\alpha$ ranged from 0 to 0.016. The (111) and (200) peaks broadened with increasing $\alpha$ and the location of the (111) shifted to higher angles while the (200) shifted to lower angles as theory predicts. Plots of the calculated intensities versus $k\alpha$ is shown in Figure 3. However, both calculated peaks shifted farther than predicted and the amount of shift was not linear with $\alpha$ as predicted by Equations 2 and 3. The peak location versus $\alpha$ is shown in Figure 4. In these calculations employing spherical geometry, $\alpha$ and the location of the stacking fault were varied simultaneously.

To investigate the effect of location of a stacking fault in a nanocrystal, a cubic model was employed. This allowed movement of the stacking fault location without a corresponding change in $\alpha$. The single stacking fault was moved incrementally in steps of one unit cell from on side of the cubic model to the other keeping $\alpha$ constant at 0.029 and the peak shifts due to stacking fault placement are shown in Figure 5. Both the (111) and (200) peaks shifted as before, with the greatest shift occurring when the stacking fault was located in the center of the cube. This demonstrates that there is a large peak shift due to the location of the stacking fault in these extremely small crystals. A third set of models were created in which a stacking fault was located at the center of a cube, but in this case only a portion of the center plane was faulted. In these models the location of the stacking fault was held constant but $\alpha$ varied from 0 to 0.029.
Figure 3: Calculated diffraction pattern from the spherical model containing a stacking fault with $\alpha=0$, 0.0083, and 0.0125.

Figure 4: Peak shift in $ka$ versus $\alpha$ in the spherical model with a stacking fault defect.

The resulting peak shifts are shown in Figure 6. With a constant stacking fault location in the nanocrystal, the peaks shift nearly linearly with $\alpha$ as predicted by Warren. The same method of expanding a stacking fault at a fixed location was used on the spherical model and the results are shown in Figure 7. The resulting peak shifts were not linear, as in the case with the cubic models, since in the spherical model the number of atoms above the faulted plane is not linear with increasing stacking fault probability. Near the ends of the sphere the stacking fault has very few atoms above the fault as compared to the center, which explains the deviation from linearity.

Twin Faults
A twin fault was placed at the center of the spherical model and the resulting calculated diffraction patterns are shown in Figure 8. No shifting of the calculated diffraction peaks was observed. However, asymmetrical broadening occurred, most notably in the (200). The lack of peak shift and the presence of asymmetrical broadening agrees with Warren's theory.

Figure 5: Peak shift in $ka$ versus stacking fault location in the cubic model. $\alpha=0.029$

Figure 6: Peak shift in $ka$ versus $\alpha$ in the cubic model with a stacking fault at a fixed location.
Conclusions

Vacancy
As a result of increasing vacancy concentration, the peak intensity decreased and the background intensity increased. These effects are consistent with theory.

Faults
In these extremely small crystals, the magnitude of the peak shift is very sensitive to location. Peak shift is also sensitive to the number of atoms above the faulted plane. Stacking and twin faults show the effects on diffraction patterns as developed by Warren.

Acknowledgment

This work was partially supported by the NSF EPSCoR Grant No. NSF-OSR-95255225.

References: