3D Analysis by Electron Diffraction
Methods of Nanocrystalline Materials

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Abstract
To analyze nanocrystalline structures quantitatively in 3D a novel
method is presented based on electron diffraction. It allows to de-
termine the average size and morphology of the coherently scattering
domains (CSD) in a straightforward way without the need to pre-
pare multiple sections. The method is applicable to all kinds of bulk
nanocrystalline materials. As an example the average size of the CSD
in nanocrystalline FeAl is determined in 3D. Assuming ellipsoidal CSD
it is deduced that the CSD have a width of 19±2 nm, a length of
18±1 nm and a height of 10±1 nm.

Keywords: nanocrystalline materials; electron diffraction; 3D analy-
sis, intermetallic FeAl, coherently scattering domain size, severe plastic
deformation

1 Introduction
Nanocrystalline materials and nanostructures receive an increasing interest
in materials science, since they often show enhanced properties (Meyers et al.,
2006). Their properties are closely linked to the 3D morphology of the nano-
structures. One widely applied approach to produce bulk nanocrystalline
structures is severe plastic deformation (SPD) of coarse grained materials car-
rried out e.g. by high pressure torsion (HPT) of bulk materials (Valiev et al.,
2006; Zhilyaev and Langdon, 2008). Systematic studies of nanostructures
are often performed using transmission electron microscopy (TEM) (Karnthaler et al., 2004) but they have not been focused on a 3D analysis, since conventional TEM analysis provides only information on a projection of the nanostructures. Especially in the case of samples made by HPT most TEM investigations have been based on plan view samples only, probably due to experimental difficulties in preparing cross-section TEM specimens of the rather thin HPT samples. Still, for nanocrystalline structures with non-equiaxed grains, the analysis of different TEM sections would be necessary for a 3D analysis of the nanostructures (Huang, 2007; Peterlechner et al., 2009). Electron back scattered diffraction is frequently applied to cross sections of HPT discs to determine the elongation of the grains (Pippan et al., 2010), however in the case of intermetallic compounds the grain size reached after HPT is too small and the dislocation density too large for the applicability of this method.

Recently tomographic methods based on TEM imaging have been developed, allowing to determine a 3D reconstruction of isolated nanostructures (e.g. nanoparticles) (Arslan et al., 2005; Midgley, 2009). These methods are rather complicated and do not allow the analysis of bulk nanocrystalline materials. They are mostly based on high-angle annular dark field imaging as diffraction contrast is not suitable for tomographic methods of crystalline materials since the diffracted intensity changes during the tilt series (Midgley, 2009). Diffraction tomography which is based on the acquisition of 3D electron diffraction data in a TEM is a very powerful tool in electron crystallography and can be used for a precise unit cell determination (Zhang et al., 2010; Kolb et al., 2007, 2008). In the present work HPT deformed bulk nanocrystalline FeAl is investigated in plan view and in cross section revealing that the grains are elongated. A novel method based on TEM diffraction has been worked out to analyze bulk nanocrystalline structures in 3D without the need to prepare several sections. This is achieved by applying profile analysis to 3D electron diffraction data.

2 Materials and Methods

A B2 ordered Fe-45at.%Al alloy was made from high purity compounds. The alloy was deformed by HPT to achieve a shear deformation \( \geq 5,000\% \) at the outer rim of the HPT samples. From the deformed samples TEM specimens were cut in two different ways: (i) plan view sections and (ii) tangential cross sections both of them correlated to the geometry of the deformed samples in a given way. The tangential cross section has its plane normal parallel to the radial direction of the HPT disc. The TEM specimens were thinned by
electropolishing and investigated in a Philips CM200 TEM equipped with a LaB$_6$-cathode, operating at an acceleration voltage of 200 kV. Recording of both, the TEM images and the selected area diffraction (SAD) patterns was done using a CCD camera. The SAD patterns were recorded from an area having a diameter of 1.2 µm. The thickness of the sample was about 82 nm in the region used for the study, as measured by EELS. In addition, energy filtered diffraction patterns were recorded on a FEI Tecnai G20 with a Gatan GIF 2001 also operating at an acceleration voltage of 200 kV and equipped with a LaB$_6$-cathode.

3 Results and Discussion

3.1 TEM investigations of plan-view and cross-section samples

Figure 1 shows a bright-field image and diffraction pattern of a TEM specimen of HPT deformed FeAl having plan-view orientation. The specimen is nanocrystalline, the grain boundaries are not well defined and the grains are about equiaxed and contain a high density of defects (cf. Fig. 1a). It should be pointed out that the contrast features observed in TEM images of nanocrystalline materials must be interpreted with special care since strong moiré contrasts can appear in overlapping nanograins (Rentenberger et al., 2004). The corresponding SAD pattern (cf. Fig. 1b) shows rings as the grain orientations are randomly distributed in the specimen; the texture is rather weak. The superlattice reflections of the B2 ordered structure (e.g. \{100\}) are absent in the diffraction pattern as the sample is chemically disordered. The loss of long range order during severe plastic deformation is frequently observed in intermetallics (Geist et al., 2010; Rentenberger and Karnthaler, 2008).

Figure 2 shows a bright-field and dark-field image of a tangential cross section of HPT deformed FeAl. The grains are elongated in the shear direction indicating that the grains have a platelet shape (cf. Fig. 1a). The platelets lie almost parallel to the shear plane in the HPT disk (their inclination angle is only $\sim 10^\circ$). The nanocrystalline grains are rather homogeneous in size, show fuzzy non-equilibrium grain boundaries and a high density of defects. An estimation of the size of the grains from the TEM images shows that the grains have a length of about $80 \pm 20$ nm and a height of around $20 \pm 10$ nm, which is in good agreement with previous studies on HPT deformed FeAl (Mangler et al., 2010).

The contrast features in the TEM bright field image of Figure 2a are
Figure 1: Top view of nanocrystalline FeAl produced by high pressure torsion. (a) TEM bright-field image and (b) corresponding diffraction pattern. Matrix reflections are indicated in bold.

Figure 2: Tangential cross-section of high pressure torsion deformed FeAl. (a) TEM bright-field image showing elongated grains. (b) In the TEM dark-field image taken from the same region small areas show up that correspond to coherently scattering domains. The shear plane is indicated by a dashed line.
complex, but when comparing them with the TEM image taken from plan view (cf. Fig. 1a) it is clearly visible that moiré effects are less dominant in the cross section image. In plan view the platelet shaped grains overlap very strongly whereas in the cross section view the platelets are standing vertically expanding in many cases through the entire TEM foil. Therefore, it can be concluded that TEM images from the cross section are necessary to study features that are linked to the shear plane.

Figure 2b shows a TEM dark field image taken from the same region as Figure 2a. The dark field image was recorded using a small section of the \{110\} reflection ring. To avoid complex contrasts from neighboring orientations, a small aperture was used for imaging (0.6 nm\(^{-1}\) diameter in reciprocal space). A comparison of the TEM bright field image with the dark field image shows that isolated regions lighting up in the dark-field image are much smaller than the grains seen in the bright-field image. Therefore it can be concluded that the grains contain substructures caused by the high density of dislocations, e.g.: small angle grain boundaries.

### 3.2 Evaluation of the CSD size by electron diffraction

Figure 3 shows the evaluation of an electron diffraction profile, that is deduced from the SAD ring pattern of a plan view sample (cf. Fig. 1b) by azimuthal integration using the software PASAD-tools (Gammer et al., 2010). Center-refinement and background subtraction were performed automatically and with high-precision using the software. The strong interaction of electrons with matter leads to a very high signal to noise ratio and thus to a smooth profile. In the diffraction profile (cf. Fig. 3a) superlattice reflections (e.g. \{100\}) are not present as the long-range order is destroyed during HPT deformation. The peaks are rather broad indicating that the coherently scattering domain (CSD) size is small.

X-ray profile analysis (XPA) is widely used for analyzing nanomaterials (Schafer and Zehetbauer, 2005). Recently it was shown that a quantitative analysis is also possible in the TEM by profile analysis based on SAD patterns (PASAD) (Gammer et al., 2010). Using X-ray methods a wide spread procedure to deduce the grain size of nanomaterials is the Williamson-Hall plot (Williamson and Hall, 1953). When plotting the peak width of the diffraction peaks against the absolute value of their diffraction vectors, the size broadening and the strain broadening can be separated. The points then lie on a straight line, where the slope of the line depends on the mean square strain and the intercept gives the size broadening of the CSD. In the modified Williamson-Hall plot the contrast factors of the dislocations (Ungar et al., 1999) are taken into account giving a better agreement (Ungar
Figure 3: (a) Diffraction profile of nanocrystalline FeAl produced by high pressure torsion. The diffraction profile was deduced from a SAD pattern taken from the plan view of the sample. (b) Corresponding modified Williamson-Hall plot. The volume weighted mean coherently scattering domain size ($\langle D \rangle_V$) can be calculated from the intercept corresponding to the size broadening.
and Borbely, 1996). It should be pointed out that for the applicability of the profile analysis based on averaging a reasonable close size distribution within the illuminated area has to be fulfilled, which is usually the case in materials made nanocrystalline by severe plastic deformation. Figure 3b shows the modified Williamson-Hall plot deduced from the electron diffraction profile shown in Figure 3a. The full width half maximum (FWHM) of the diffraction peaks were deduced by fitting pseudo-Voigt functions to all the peaks using the PASAD-tools. From the size broadening ($\Delta g_{size}$), the volume weighted mean CSD size ($\langle D \rangle_V$) is determined using the equation: $\langle D \rangle_V = 0.9 \cdot (\Delta g_{size})^{-1}$ (Williamson and Hall, 1953). From this analysis a resulting $\langle D \rangle_V = 20 \pm 2$ nm is deduced. (The error was calculated from the fit.)

All FWHM values were deconvoluted for the instrumental peak broadening using Voigt deconvolution. The deconvolution was performed by recording a diffraction pattern from a single crystalline sample using the same parameters and fitting pseudo-Voigt functions to the diffraction spots. It should be mentioned that there was no significant variation in the width of the diffraction spots or central beam, indicating that there is no significant dependence of the instrumental broadening on the diffraction angle. The FWHM of the instrumental broadening was 0.0305 nm$^{-1}$ in the present case.

To check the dependence of the CSD size on the acquisition parameters, SAD patterns were recorded from sample areas with different thicknesses and using different illuminated areas. The results did not differ significantly, but by using thicker samples an increased background can be noted. The area of diffraction that can be used is limited by the maximum size of parallel illumination in the TEM.

To exclude any influence of inelastic scattering on the measured peak width energy filtered SAD patterns were recorded with a slit width of 1 eV for both, an untitled position and a position where the sample was tilted to $+30^\circ$. Integrating the entire SAD pattern, the volume weighted mean CSD size was determined. For a comparison the energy filter was switched off and the measurement was repeated. As shown in Table 1, the values measured on the Tecnai G20 lie within the errors of the values obtained on the CM200 when the instrumental peak broadening is taken into account. This indicates that neither energy filtering nor the microscope used have much influence on the results of the measured CSD size. It should be mentioned however that energy filtering leads to a reduction of the background in the diffraction profile. This might be beneficial for complicated profiles with overlapping peaks, where it is not straightforward to subtract the background.
Table 1: Comparison of the volume weighted mean CSD size obtained from different microscopes at two different tilt positions

<table>
<thead>
<tr>
<th>Microscope</th>
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<th>tilted to +30°</th>
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<tbody>
<tr>
<td>CM200</td>
<td>20 ± 2 nm</td>
<td>18 ± 1 nm</td>
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<tr>
<td>G20</td>
<td>20 ± 1 nm</td>
<td>17 ± 2 nm</td>
</tr>
<tr>
<td>G20, energy filtered</td>
<td>19 ± 2 nm</td>
<td>18 ± 2 nm</td>
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3.3 3D analysis by electron diffraction

Figure 4a shows a proposed average shape of a CSD. From the top view the CSD is equiaxed whereas in the cross-section it is elongated. The value of $\langle D \rangle_V$ deduced from the profile analysis represents the CSD size parallel to the diffraction vector, i.e. the volume weighted size of horizontal cuts through the CSD. When the CSD is untilted, it is cut through its longest axes and the resulting $\langle D \rangle_V$ value has its maximum. When tilting the sample (cf. Fig. 4b), the value of $\langle D \rangle_V$ is reduced.

To obtain a quantitative information on the average CSD size in 3D it is necessary to analyze each SAD pattern along the tilt axis and the axis normal to that separately. As shown in Figure 4a and b, $\langle D \rangle_V$ measured along the tilt axis (indicated by f) does not change when tilting the sample, whereas for an elongated CSD $\langle D \rangle_V$ measured along the axis normal to the tilt axis (indicated by e) is reduced. Therefore, two sets of diffraction profiles were deduced from selected regions of the SAD patterns only. As shown in Figure 4c a region of 10 degrees around the tilt axis was taken into account and in addition a region around the axis normal to that. For both sets of diffraction profiles a modified Williamson-Hall plot was used to determine the volume weighted mean CSD size.

Figure 5a shows the plot of $\langle D \rangle_V$ measured in the direction normal to the tilt axis as a function of the tilt angle. A plan view specimen (cf. Fig. 1) was used and SAD patterns were recorded within a large range of tilt angles: Tilting angles of the incident beam ranging from $-52.5^\circ$ to $+52.5^\circ$ in steps of 5° were applied. Assuming that the CSD has an ellipsoid shape allows to calculate the variation of $\langle D \rangle_V$ with the tilt angle. The model for ellipsoidal shaped CSD is fitted to the experimental data (cf. solid line in Fig. 5a) showing a good agreement. From the fit it is deduced that the platelet shaped CSD have a length of 18±1 and a height of 10±1 nm. This leads to an aspect ratio of 1.8. Figure 5b shows the plot of $\langle D \rangle_V$ against the tilt angle for the measurement along the tilt axis. The data show some scattering but no trend can be deduced. As expected, $\langle D \rangle_V$ measured along the tilt axis does not change when tilting. The mean of all data points is 19±2 nm.
Figure 4: Schematic representation of a platelet shaped ellipsoidal CSD. The effect of tilting on the measured volume weighted mean coherently scattering domain sizes ($\langle D \rangle_V$) is shown. (a) $\langle D \rangle_V$ measured in the direction of the tilt axis $f$ and the direction normal to that $e$ are shown. (b) Tilting the sample leads to a reduction of $e$ whereas $f$ stays constant. (c) The regions of the SAD pattern used for the evaluation of $e$ and $f$ are shown.
Therefore it can be deduced from the diffraction analysis that the assumption of an ellipsoid average shape for the CSD is valid and that the CSD has a width of 19±2 nm, a length of 18±1 nm and a height of 10±1 nm.

The method presented here allows to determine the average width of the CSD in 3D by evaluating the SAD pattern along different directions with respect to the tilt axis for a large range of tilt angles. The fact that $\langle D \rangle_V$ measured along the tilt axis does not change when tilting while a large change is seen when measuring along the axis normal indicates the validity of the method. While the elongation of the average CSD size could have been determined by using less tilting angles, the fine sampling has the advantage of reducing the error of the overall measurement. Using TEM for the diffraction experiment allows a quick and automatic acquisition of tilt series due to the short exposure time needed to collect diffraction patterns and the possibility to use scripting for the microscope control (Kolb et al., 2007).

The quantitative 3D result of Figure 5 confirms the estimate resulting of the dark field image of the specimen with cross section view (cf. Fig. 2b). The result that the dimensions of the CSD are smaller and less elongated than those of the grains is related to the occurrence of substructures (e.g.: small angle grain boundaries) that fragment the elongated grain into smaller less elongated CSD. Also the present results of FeAl agree with those of Ti (Zhu et al., 2003) indicating that in nanocrystalline materials produced by severe plastic deformation it is important to distinguish between CSD and grain sizes.

3.4 Applicability of 3D profile analysis

The method presented here is different from 3D reconstructions using tomography methods found in the literature. These methods are based on TEM images showing a contrast that is a monotonic function of some physical property (e.g. mass diffraction contrast as in the case of biological specimens). In these cases the sample is tilted and images are recorded thus allowing to reconstruct isolated or embedded nanostructures. Still these methods can not be applied to nanocrystalline materials as their contrast is dominated by the specific diffraction condition during the tilting series. In contrast the method presented here is based on electron diffraction and allows the reconstruction of the size and shape of the average coherently scattering domain. It should be noted that the evaluation of $\langle D \rangle_V$ is based on the fact that a large number of CSD is present in the illuminated area. The set of CSD that contributes to the broadening of a diffraction peak changes with the tilt position since tilting leads to a change of the diffraction condition. But the information that is obtained only from the set of CSD having a reflecting plane near Bragg
Figure 5: Variation of the volume weighted mean coherently scattering domain (CSD) sizes ($\langle D \rangle_V$) with the tilt angle. (a) $\langle D \rangle_V$ measured along the axis normal to the tilt axis (cf. axis $e$ in Fig. 4). The line is calculated for ellipsoidal CSD and shows good agreement to the experimental data. (b) $\langle D \rangle_V$ measured along the tilt axis (cf. axis $f$ in Fig. 4). No clear trend of the change with the tilt angle is observed. The solid line represents the mean value.
condition is sufficient due to the large number of CSD present. Therefore, the method is applicable to all kinds of nanocrystalline materials allowing to determine the average size and morphology of the CSD without the need to prepare multiple sections.

Analyzing the CSD sizes statistically directly from the TEM images would not have been an alternative because complex contrast features are frequently observed in TEM images of bulk nanocrystalline materials due to high dislocation densities in the fragmented grains and strong moiré effects of overlapping nanograins or CSD (Rentenberger et al., 2004). Therefore, the segmentation of the CSD in the dark-field images can be quite difficult. In contrast grain sizes can only be determined from TEM images. Therefore the possibility of the TEM to switch between imaging and diffraction mode allows to acquire information on both, the CSD size and the grain size. The diffraction technique described here is an averaging technique, although this allows a good statistic it does not have the sensitivity of electron tomography with respect to different sizes and morphologies. Still, by using SAD it is possible to get local quantitative information of areas selected in TEM images which is necessary when using non-homogeneous nanocrystalline materials that are frequently present after severe plastic deformation of intermetallic compounds (Gammer et al., 2010). The method presented here can be used to analyze the evolution of the elongation of the average CSD in FeAl during high pressure torsion deformation from the early stages of the formation of small nanocrystalline volumes that are formed in the material until the saturation is reached (Gammer et al., 2010). This could give additional information on the deformation mechanisms during high-pressure torsion.

4 Conclusions

- Electron diffraction at different tilt positions of the sample can be used to reconstruct the average size and shape of the coherently scattering domains on a local scale. The average size can be obtained by measuring the peak width of diffraction rings along certain directions.

- In contrast to standard tomography, the method can be applied to bulk nanocrystalline materials.

- The method was successfully applied to FeAl made nanocrystalline by severe plastic deformation showing that the coherently scattering domains have an elongated shape parallel to the shear plane.

- A comparison with TEM images obtained from the cross section show
that the dimensions of the average CSD are smaller and less elongated than those of the grains indicating the occurrence of substructures.

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