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Determining the radial pair-distribution function within intergranular amorphous films by numerical nanodiffraction

C.T. Koch[a,*], S.H. Garofalini[b]

[a]Max Planck Institute for Metals Research, Heisenbergstr. 3, D-70569 Stuttgart, Germany
[b]Rutgers University, Piscataway, NJ 08854-8065, USA

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Abstract

We report on an alternative method to electron nanodiffraction and fluctuation microscopy for the determination of the reduced density function $G(r)$ of amorphous areas with small cross-sections. This method is based on the numerical extraction of diffraction data from the complex-valued exit-face wave function as obtained by HRTEM focal series reconstruction or electron holography. Since it is thus possible to obtain "diffraction data" from rectangular areas of any aspect ratio, this method is particularly suited for intergranular glassy films of only 1−2 nm width, but lengths of several 100 nm. A critical comparison of this method with the already established nanodiffraction and fluctuation microscopy will be made.

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1. Introduction

The presence of intergranular glassy films (IGFs) in polycrystalline ceramics, such as silicon nitride [1], alumina [2], or silicon carbide [3] strongly affects their mechanical (e.g. fracture toughness, creep resistance), chemical, and electrical properties. Understanding the structure of such amorphous films at the atomic level will make the comparison with theoretical models and thus intelligent design of these materials possible. A very useful tool for the structural characterization of amorphous structures are pair-distribution functions reflecting the number of atom-pairs of certain species per unit volume that are a given distance apart from one another. While diffraction experiments are insensitive to the absolute position of the diffracting object, they are very sensitive to the relative distance between 2 objects simultaneously diffracting a coherent incident wave, making them an ideal tool to study pair-distribution functions of amorphous structures. The scattering of neutrons and X-rays is, in addition to atom core mass and electron charge density, also sensitive to spin and polarization of the incident radiation, respectively. It is thus possible to perform a series of different scattering experiments in order to determine partial pair-distribution functions, one for each pair of atom species. Since the elastic scattering of electrons is only determined by the scalar electrostatic potential, this additional degree of freedom does not exist. The only chance to determine partial pair-distribution functions using elastically scattered electrons is to make use of the different dependence of the atomic scattering factors on the scattering angle, e.g., at high angles the scattering is dominated by heavy atoms. Since such an analysis requires very high quality data and may not work for all atom pairs, it is thus generally only possible to determine the weighted sum of partial pair-distribution functions, the reduced density function

$$G(r) = 4\pi r[\rho^R(r) - \rho_0], \tag{1}$$

from electron diffraction data [4]. Here ρ_0 is the mean atom density and $\rho^R(r)$ is an inter-atomic distance-dependent atom density term. Dynamic scattering effects may

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*Corresponding author. Tel.: +49 711 689 3647; fax: +49 711 689 3522.
E-mail address: koch@mf.mpg.de (C.T. Koch).

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complicate the data analysis even further, requiring very thin specimen to be used for this method [4].

The structure factor $F(\vec{q})$ of an amorphous structure containing N_{atom} atoms is defined at the reciprocal space point $\vec{q}$ as

$$F(\vec{q}) = \sum_{j=1}^{N_{\mathrm{atom}}} f_j(|\vec{q}|)\exp[2\pi \mathrm{i}\vec{q}\cdot\vec{r}_j], \tag{2}$$

where $\vec{r}_j$ is the real-space position of atom j and $f_j(|\vec{q}|) = f_j(q)$ its (isotropic) atomic scattering factor. Within the kinematic scattering approximation the resulting diffraction pattern is

$$I(\vec{q}) = |F(\vec{q})|^2 = \sum_{j=1}^{N_{\mathrm{atom}}} f_j(q)^2 + \sum_{j=1}^{N_{\mathrm{atom}}}\sum_{l\neq j} f_j(q) f_l(q)\exp[2\pi \mathrm{i}\vec{q}\cdot\vec{r}_{jl}], \tag{3}$$

where $\vec{r}_{jl} = \vec{r}_j - \vec{r}_l$.

If all atoms are of the same species, i.e. $f_i(q) = f_l(q)$ for all $i, l = 1\ldots N_{\mathrm{atoms}}$, we may write $f_i(q)f_l(q) = \tilde{f}(q)^2$ and obtain a two-dimensional atom density correlation function

$$g(\vec{r}) = \mathrm{FT}^{-1}\left\{\left[I(\vec{q}) - \sum_{i=1}^{N_{\mathrm{atom}}} f_i(q)^2\right]\Big/\tilde{f}(q)^2\right\} = \sum_{j=1}^{N_{\mathrm{atom}}}\sum_{l\neq j}\delta(\vec{r}-\vec{r}_{jl}). \tag{4}$$

For multi-component materials, i.e. if not all scattering factors are identical the right-hand side of above equation will, due to differences between $\tilde{f}(q)$ and $f_j(q)$, slightly deviate from a sum of perfect delta-functions. In this case $\tilde{f}(q)$ is, just as in direct methods [5] a generalized atomic scattering factor which may be approximated by the average scattering factor of all atoms in the scattering volume.

$$\tilde{f}(q)^2 = \frac{1}{N_{\mathrm{atom}}^2 - N_{\mathrm{atom}}}\sum_{j=1}^{N_{\mathrm{atom}}}\sum_{l\neq j} f_j(q) f_l(q). \tag{5}$$

In this paper we determine $\tilde{f}(q)$ by fitting $\sqrt{I(q)}$ with a sum of 4 Gaussians which is the standard parameterization for atomic scattering factors introduced by Doyle and Turner [6].

The reduced density function $G(r)$ is now given by the azimuthal integral

$$G(r) = \int_0^{2\pi} g(\vec{r})r\,\mathrm{d}\phi. \tag{6}$$

This function may, alternatively, also be obtained by performing a one-dimensional inverse Fourier transform on the azimuthally integrated intensity in the diffraction pattern [4].

Despite a number of disadvantages of using electrons versus other radiation for the analysis of amorphous structures mentioned in the introduction, one of their great advantages lies in their focusability to small probes, allowing the examination of very small volumes of material such as IGFs. Recently, McBride and Cockayne [7] have been able to obtain $G(r)$ of IGFs by electron nanodiffraction with probe sizes of $d_{\mathrm{spot}} = 2\,\mathrm{nm}$. As a result of Heisenberg's uncertainty principle, the very high resolution in real-space results in a reduced reciprocal-space resolution. Convergent illumination of the specimen is required to form a $d_{\mathrm{spot}} = 2\,\mathrm{nm}$ wide probe, which means that the resulting diffraction pattern $I'(\vec{q})$ is convoluted with a top-hat aperture function $p(\vec{q})$ whose width is inverse proportional to the size of the probe in real-space (e.g. 0.85 mrad convergence semi-angle at 297 kV for 2.0 nm spot FWHM [7]). This increases the reciprocal-space sampling interval with which independent data points can be collected from the diffraction pattern. The sampling of the diffraction data is again inversely proportional to $r_{\max}$, the range of r over which $G(r)$ allows any meaningful interpretation, so that

$$r_{\max} \leqslant c d_{\mathrm{spot}}, \tag{7}$$

where $c<1$. For an ideal point-like electron source, an ideal (aberration free) illumination system, the collection of very large scattering angles, the absence of thermal diffuse scattering, and $\tilde{f}(q) = \mathrm{const}$, i.e. no specimen-related attenuation of the scattering signal and the related decrease in signal-to-noise ratio for large scattering angles we may assume $c = 1$, but only, if we allow probe sidelobes to cover an area much larger than d_{spot}. Since these are not realistic assumptions McBride et al. [8] have used deconvolution to reconstruct the diffraction pattern $I(\vec{q})$ from $I'(\vec{q}) = I(\vec{q}) \otimes p(\vec{q})$ in order to enhance its reciprocal-space resolution. However, deconvolution only works if the probe may be treated as being incoherent and it also enhances noise present in the data. The usability of the deconvoluted data thus depends strongly on the noise level and the degree of coherence of the probe forming electron beam. An electron probe of the size of only 1 nm requires at least partially coherent illumination, which was the reason why McBride et al. [9] have investigated the effects of coherence on the quality of the retrieved $G(r)$, finding that for sufficiently large electron probes ($\geqslant$1.2 nm FWHM) the coherence effects may be suppressed. The same problem is faced by fluctuation microscopy [10], where a series of hollow-cone images of different precession angles are combined to provide a spatially resolved $I(q)$ map. The inverse of the size of the objective aperture used to select the range of scattering angles forming these images defines their real-space resolution.

The "$\leqslant$" relation has been used in expression (7), because we have so far only been talking about the upper limit of $r_{\max}$ imposed by the illumination geometry. Dynamic scattering effects and differences in atomic scattering factors further limit the range over which $G(r)$ is interpretable.

IGFs only impose a real-space constraint in the direction normal to the film but not along it. It might therefore be