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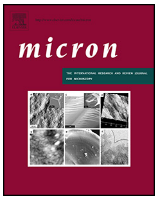

The effect of probe inaccuracies on the quantitative model-based analysis of high angle annular dark field scanning transmission electron microscopy images

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ARTICLE INFO

Article history:
Received 20 September 2013
Received in revised form
13 December 2013
Accepted 15 December 2013

Keywords:
HAADF STEM
Probe aberrations
Statistical parameter estimation theory
STEM simulations

ABSTRACT

Quantitative structural and chemical information can be obtained from high angle annular dark field scanning transmission electron microscopy (HAADF STEM) images when using statistical parameter estimation theory. In this approach, we assume an empirical parameterized imaging model for which the total scattered intensities of the atomic columns are estimated. These intensities can be related to the material structure or composition. Since the experimental probe profile is assumed to be known in the description of the imaging model, we will explore how the uncertainties in the probe profile affect the estimation of the total scattered intensities. Using multislice image simulations, we analyze this effect for *Cs* corrected and non-*Cs* corrected microscopes as a function of inaccuracies in cylindrically symmetric aberrations, such as defocus and spherical aberration of third and fifth order, and non-cylindrically symmetric aberrations, such as 2-fold and 3-fold astigmatism and coma.

1. Introduction

The use of a high angle annular dark field detector in a scanning transmission electron microscope (HAADF STEM) allows one to obtain images whose contrast is sensitive to structural and chemical information of the material under study. The intensities of these images scale with the mean atomic number *Z* of the atomic columns, hence the name *Z*-contrast imaging (Pennycook and Jesson, 1991). It has also been demonstrated that the intensities can be related to the number of atoms present in each atomic column (Van Aert et al., 2011, 2013; LeBeau et al., 2010; De Backer et al., 2013). Therefore, this technique is widely used for chemical and structural analyses of materials at the atomic level. To analyze HAADF STEM images as accurately and precisely as possible, quantitative methods are needed. In order to analyze HAADF STEM images quantitatively, several approaches have been proposed (Rosenauer et al., 2009; Robb et al., 2012; LeBeau et al., 2008; Kotaka, 2010). Furthermore, statistical parameter estimation theory has been introduced as an alternative method to extract quantitative information from HAADF STEM images, such as chemical composition (Van Aert et al., 2009; Martinez et al., 2014) or number of atoms (Van Aert et al., 2011, 2013; De Backer et al., 2013), with high accuracy and precision. In this framework, HAADF STEM images are described using a simplified parameterized empirical imaging model. The unknown parameters of this model are then estimated in an iterative way by fitting this model to the experimental images using a criterion of goodness of fit, such as least squares, least absolute squares or maximum likelihood (den Dekker et al., 2005; Van Aert et al., 2005). In this manner, the total intensity of scattered electrons can be quantified atomic column-by-atomic column, which is particularly interesting due to its sensitivity for the chemical composition. The use of this methodology has been shown to allow for a chemical quantification of interfaces (Van Aert et al., 2009), and to study the structure and composition of nanoparticles (Bals et al., 2011) and nanoclusters (Bals et al., 2012). The research on nanostructured materials such as nanoparticles is of great interest because of their wide applications in different fields, such as catalysts for example (Yu et al., 2012). Model-based quantification of HAADF STEM images has been presented in Van Aert et al. (2009, 2012) and an extensive analysis on the inherent limitations of this methodology as a tool for atom counting has been explained in De Backer et al. (2013). Furthermore, the model assumptions and validity for single atomic column chemical quantification have been discussed in Martinez et al. (2014). In this work, we analyze how inaccuracies in the probe aberrations, which are usually assumed to be known, affect the estimation of the scattered intensities of the atomic columns. For that purpose, we will make use of multislice simulations under the absorptive potential

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0968-4328/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.micron.2013.12.009

approach (Ishizuka, 2002) because of their suitability to describe electron-sample interactions for thin samples. In Section 2, we will review the model-based analysis for quantification of HAADF STEM images. In Section 3 we will describe the simulation methodology and settings. We consider the example of Pt as a test material because of its increasing interest in the catalyst research community (Chen and Holt-Hindle, 2010). However, the analysis can be extended to all types of materials. In Section 4, the results will be presented and discussed. Finally, in Section 5, conclusions are drawn.

2. Model-based parameter estimation

Model-based electron microscopy has recently been reviewed in Van Aert et al. (2012), where a wide scope of applications is discussed as well. For the particular case of quantification of Z-contrast HAADF STEM images, the methodology is presented in Van Aert et al. (2009). Quantitative information is then obtained by measuring total scattered atom column intensities using statistical parameter estimation theory. An empirical incoherent imaging model is used to measure these quantities. This parametric model describes the expectations of the pixel values of the HAADF STEM image. If we assume an incoherent model for this purpose, we can describe the electron-sample interaction as the convolution between an object function and the probe intensity (Pennycook and Jesson, 1991; Nellist, 2007):

$$f_{kl}(\boldsymbol{\theta}) = f(\mathbf{r}_{k,l};\boldsymbol{\theta}) = \mathrm{O}(\mathbf{r}_{k,l};\boldsymbol{\theta}) * \mathrm{P}(\mathbf{r}_{k,l}) \tag{1}$$

where $\mathrm{O}(\mathbf{r};\boldsymbol{\theta})$ is the object function depending on the unknown structure parameters $\boldsymbol{\theta}$ and $\mathrm{P}(\mathbf{r})$ is the probe function depending on a set of probe parameters including acceleration voltage, defocus, aperture semi-angle, spherical aberration constant and high order aberration coefficients. The indices (k, l) correspond to the STEM probe at position $\mathbf{r}_{k,l} = (x_k\, y_l)^T$.

The information about the sample and the HAADF detector is incorporated in the object function, which describes the scattering interaction of the probe with the projected potential recorded at the detector plane. This function is sharply peaked at the atom column positions and can be defined as a superposition of Gaussian peaks:

$$\mathrm{O}(\mathbf{r}_{k,l};\boldsymbol{\theta}) = \zeta + \sum_{n=1}^{N} \eta_n \exp\left(\frac{-(x_k - \beta_{x_n})^2 - (y_l - \beta_{y_n})^2}{2\rho^2}\right) \tag{2}$$

where ζ is a constant background, N is the total number of atomic columns to be analyzed, ρ is the width of a Gaussian peak, η_n is the height of the nth Gaussian peak, β_{x_n} and β_{y_n} are the x- and y-coordinates of the nth atomic column, respectively.

Thus, the unknown parameters are given by the parameter vector:

$$\boldsymbol{\theta} = (\beta_{x_1}, \ldots, \beta_{x_N}, \beta_{y_1}, \ldots, \beta_{y_N}, \rho, \eta_1, \ldots, \eta_N, \zeta)^T \tag{3}$$

In order to estimate the unknown parameters, use is made of the uniformly weighted least squares estimator. The function parameters are then estimated by minimizing the least squares sum using an iterative routine. After the estimation of the unknown parameters from the experimental images, the volumes under the Gaussian peaks above the background are used as a sensitive measure to extract quantitative information. It has been shown that this measure is proportional to the total intensity of electrons scattered by a specific atomic column that was integrated at the HAADF detector (Van Aert et al., 2009). These volumes can be computed as follows:

$$\mathrm{V}_n = 2\pi\eta_n\rho^2 \tag{4}$$

The function $\mathrm{P}(\mathbf{r})$ in Eq. (1) is the STEM probe that scans over the sample. It is given by the following expression:

$$\mathrm{P}(\mathbf{r}) = |p(\mathbf{r})|^2 * S(\mathbf{r}) \tag{5}$$

where $|p(\mathbf{r})|^2$ is the coherent point source contribution and $S(\mathbf{r})$ represents the incoherent source size effects (Born and Wolf, 1998). The STEM probe formation takes place at the objective lens, which strongly focuses the electron beam to form a crossover which is described by the function $p(\mathbf{r})$. This function is given by the inverse Fourier transform of the transfer function of the objective lens $T(\mathbf{g})$, which is defined as:

$$T(\mathbf{g}) = A(\mathbf{g})\exp(i\chi(\mathbf{g})) \tag{6}$$

with $A(\mathbf{g})$, the so-called aperture function, being a circular top-hat function with unity height and radius g_{ap}. The objective aperture semi-angle α_0 is related to this function by the equality $\alpha_0 = g_{ap}\lambda$, where λ is the electron wavelength. The exponential term in Eq. (6) describes a phase shift $\chi(\mathbf{g})$ due to the objective lens aberrations. The function $\chi(\mathbf{g})$ incorporates the effect of rotationally symmetric aberrations, such as defocus and spherical aberration of third and fifth order. Non-symmetric aberrations such as astigmatism and coma can also be included in this function for a more accurate description of the probe profile (Haider et al., 2000). Extensive work has been performed in order to measure the objective lens aberrations (Haider et al., 2000; Wong et al., 1992; Uhlemannm and Haider, 1998; Batson, 2006; Krivanek et al., 2008). The most recent aberration corrected instruments incorporate automated routines to measure the residual aberrations on a daily basis. Computer assisted routines have been developed to analyze diffractogram tableaus, so-called Zemlin-tableaus (Zemlin et al., 1978), and to address residual aberrations and their stability during the experiment (Barthel and Thust, 2010). For STEM, use is made of far-field shadow images, so-called Ronchigrams, to perform this task (Lupini et al., 2010). The parametric model proposed in Van Aert et al. (2009) assumes the probe function to be known. This probe function is determined by the instrument. The characteristic probe aberrations should be measured experimentally. Residual aberrations can be measured with different methodologies up to the unavoidable experimental limitations, including reading noise, fluctuations of the probe current due to microscope instabilities, hardware and software computational restrictions (Barthel and Thust, 2010). Thus, there is an unavoidable uncertainty in the probe profile. Therefore, we will study how these inaccuracies affect the parameter estimates, the scattered intensities given by Eq. (4), in particular. We will show our analysis as a function of inaccuracies in defocus (C_1), spherical aberration of third (C_3) and fifth order (C_5), 2-fold (A_1) and 3-fold (A_2) astigmatism and coma (B_2).

3. HAADF STEM simulation study

The analysis presented in this work will make use of multislice simulations under the absorptive potential approximation (Ishizuka, 2002) using the StemSim software (Rosenauer and Schowalter, 2007). The absorptive potential approximation is computationally less demanding while it still describes the image intensities properly up to 50 nm thickness of the sample (Rosenauer et al., 2009). We simulated a Pt structure in [1 0 0] and [1 1 0] zone axis up to 75 atoms thickness, that is, ≈30 nm and ≈21 nm, respectively. The simulated images were convolved with a Gaussian function to account for spatial incoherence. We consider two cases: a *Cs* corrected and a non-*Cs* corrected microscope under their corresponding Scherzer conditions. The simulation settings are summarized in Table 1.

Using the theory described in Section 2, the scattered intensities, given by Eq. (4), have been estimated from the simulated images

Please cite this article in press as: Martinez, G.T., et al., The effect of probe inaccuracies on the quantitative model-based analysis of high angle annular dark field scanning transmission electron microscopy images. Micron (2014), http://dx.doi.org/10.1016/j.micron.2013.12.009