Three-dimensional morphology of cementite in steel studied by X-ray phase-contrast tomography

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We show that non-destructive, in-line X-ray phase-contrast tomography (PCT) can be used to study the three-dimensional morphology of individual cementite particles in steel with a spatial resolution of approximately 1.5 µm in a sample volume of 600 × 400 × 250 µm³. The smallest detectable cementite grains are 5 µm in size. The PCT results correspond very well to optical microscopy in combination with serial sectioning. We estimate the temporal resolution of PCT for in situ studies of cementite to be 30 min.

Keywords: Cementite; Heat-resistant steels; Phase transformation kinetics; Synchrotron radiation

The morphology of cementite in steel has a large effect on the mechanical properties of steel [1], which is the reason for studies world-wide into the three-dimensional (3D) morphology of cementite [2–6]. The morphology of cementite in steel can be divided into three main categories: (1) large (few to tens of micrometers) spherical-like particles of cementite in a matrix of ferrite or austenite; (2) lamellae of cementite in pearlite; and (3) carbides (nanometer to submicron particles) of cementite in bainite and in tempered martensite. Spheroidization of cementite is an example of an important industrial process, e.g. in the production of rolling bearings, in which the lamellae of cementite in pearlite are transformed into spheres of cementite with the aim of facilitating machining, and warm- and cold-forming operations of the steel.

Studying the evolution of the morphology of cementite in 3-D during spheroidization is challenging, because current state-of-the-art techniques require destructive serial sectioning [2–6], which has the intrinsic limitation that the evolution of individual cementite particles cannot be studied. Only the average growth behaviour of cementite particles can be studied by serial sectioning. Moreover, the holes present in naturally grown cementite lamellae also need to be investigated, because the work of Wang [2] has shown that these intrinsic holes play an important role in the initiation and development of pearlite spheroidization.

The density difference of 3% between cementite and ferrite is too small to distinguish cementite by conventional X-ray attenuation-contrast tomography. The aim of our research is to determine the feasibility of studying the 3D morphology of cementite in steel by using X-ray phase-contrast tomography (PCT). The two main advantages of PCT compared to diffraction-based methods, i.e. 3D X-ray diffraction (XRD) and diffraction contrast tomography (DCT) [7], are that: (1) the number of projections from an individual cementite grain is in the case of PCT much higher (determined by the number of rotation steps) than in the case of 3DXRD and DCT (determined by the number of times that the cementite grains reflect the radiation during rotation), which results in a higher spatial resolution of the reconstructed interface between the ferrite matrix and the cementite particles, and (2) PCT can deal with a very large number of cementite grains in a relatively large matrix of ferrite without the need for beam-scanning techniques. Compared to DCT, PCT has the additional advantage that PCT can also be used when the cementite particles are slightly deformed.

The specimens in our study were manufactured from steel with the following composition (in wt.%): 0.6 C, 0.6...
Mn and 2.8 Cu. The steel sample was annealed in vacuum of 10^{-5} mbar at constant temperature of 700 °C for times varying between 1 and 70 h. Annealing was followed by cooling to room temperature at a rate of 2 °C min^{-1}. Cementite structures corresponding to different annealing times were studied using light microscopy and serial sectioning with a step size of approximately 2.5 μm. Figure 1 shows that cementite grains vary in size between one and tens of micrometers depending on the duration of the treatment. The specimens for the PCT measurements are 200–400 μm thick.

The phase-contrast imaging experiments were performed at the materials science beamline ID11 of the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). Beamline ID11 is based on an undulator X-ray source that produces a quasi-parallel beam with a source size of full width at half maximum (FWHM) = 57 × 10 μm² (H × V). The X-ray beam is monochromatized to an X-ray energy of 40 keV using a Laue–Laue crystal with an energy bandwidth ΔE/E = 10^{-4}. We used the first experimental station, which allows a source-to-detector distance of 48 m, corresponding to a spatial coherence length of approximately 9 × 50 μm² (H × V). A FReLoN 2k CCD detector was coupled to a 30 μm thick scintillator via a 20× magnification objective lens. The resulting spatial resolution was estimated from the acquired images by estimating its point spread function; it resembles a Gaussian with a FWHM of approximately 1.4 μm. For each tomographic acquisition series 1200 projections were recorded uniformly spaced over the full 360° angular range. The projections were acquired in the format of 1024 × 1024 with a pixel size of 0.75 μm at three different sample-to-detector distances: 3, 68 and 208 mm.

Phase-contrast imaging is based on Fresnel diffraction of light at the inhomogeneities of the electron density within the specimen [8]. Ferrite and cementite have different electron densities, mainly due to the high carbon content in the cementite. As a result, X-rays are diffracted at the interfaces between the cementite and ferrite. If the specimen is illuminated with a monochromatic coherent beam, Fresnel diffraction rings can be observed around the boundaries of the cementite grains when a detector is placed at a sufficiently large distance behind the specimen. The recorded image that contains such a diffraction signal can be used to identify cementite structures, see Figure 2. Furthermore, an electron-density map of the specimen can be calculated using so-called phase-retrieval techniques [9–12] followed by tomographic reconstruction, see Figure 2.

All recorded images were pre-processed with a standard dark-field correction method using a dark-field reference image acquired once per tomographic dataset. Slow variations in the illumination of the specimen were corrected using reference flat-field images acquired after every 100 projections, while rapid variations were corrected in each projection using a flat-field that was estimated from the non-attenuated pixel values beside the object.

A recorded phase-contrast image of the cementite is often contaminated by so called extinction spots—areas on the image with low intensity due to diffraction of the incoming X-ray beam by the atomic lattice of a ferrite grain. Each extinction spot occurs only in those projections in which the orientation of the grain with respect to the incoming beam corresponds to the Bragg diffraction angle. That property allows us to reduce significantly the effect of extinction spots. The intensity variations caused by the Bragg diffraction can be estimated by applying a high-pass filter to the sinogram along the angular dimension and a low-pass filter along the spatial dimensions. The estimated intensity of the extinction spots can be then subtracted from the sinogram.

Misalignments between the projections in a sinogram reduce the quality of subsequent tomographic reconstruction. Such misalignments were estimated from the acquired data and did not exceed ~1 μm throughout the complete dataset. A procedure described in Ref. [13] was applied to the data in order to compensate for the misalignments between the projections.

A linear approximation to Fresnel diffraction [8] yields the so-called Mixed TIE-CTF model (transport of intensity equation–contrast transfer function) for in-line phase-contrast imaging. It is based on the assumption that the phase image of the specimen ϕ(x) is sufficiently smooth:

Figure 1. Light microscopy of the cementite–ferrite structure in steel specimens annealed at a temperature of 700 °C for (a) 1, (b) 10, (c) 20 and (d) 70 h.

Figure 2. A single slice of the tomographic reconstruction of the steel specimens annealed for 20 h (a and c) and 70 h (b and d). (a) and (b) Show reconstructions based on raw phase-contrast data (no phase retrieval); (c) and (d) show electron density reconstructions based on phase-retrieved images.
\[ |\phi(x) - \phi(x + \lambda R u_{\text{max}})| \ll 1, \]  
(1)

where \( \lambda \) is the wavelength of the monochromatic X-ray beam, \( R \) is the object–detector distance and \( u_{\text{max}} \) corresponds to the maximal spatial frequency contained in the recorded phase image. This approximation breaks down around steel–air interfaces, including the outside boundaries and the pores of the specimen. It is, however, valid for the ferrite–cementite interfaces and should provide a correct image of the cementite grains away from the specimen boundaries. The observed image can be described in Fourier space as a combination of an attenuation term and a phase term:

\[ \hat{F}(I_R) = \cos(\lambda R u^2) \cdot \hat{F}(I_0) + \sin(\lambda R u^2) \cdot \hat{F}(I_0 \phi) \]  
(2)

where \( \hat{F}(I_R) \) is the Fourier transform of the image observed at an object–detector distance \( R \) using a monochromatic light of wavelength \( \lambda \), \( u \) represents the spatial frequency, \( I_0 \) is the attenuation image of the object at \( R = 0 \), and \( \phi \) is the projected phase image of the object at \( R = 0 \). At a distance \( R \) equal to zero, only the attenuation image of the object will be observed: \( \hat{F}(I_R) = \hat{F}(I_0) \). When the distance \( R \) is large, the second term, which corresponds to the phase-contrast contribution, will appear. Unfortunately, when the object–detector distance is increased, the second term in Eq. (2) only produces high contrast in a limited range of spatial frequencies, namely when \( 0 < \lambda R u^2 < 1 \). The second term will reduce to zero at a set of spatial frequencies \( \lambda R u^2 = 0, 1, 2, \ldots \) and is attenuated by an envelope as a result of the finite source size and a finite detector resolution. In practice, it is often infeasible to reconstruct the image at spatial frequencies \( \lambda R u^2 > 1 \). The latter determines how much the phase contrast can be enhanced by allowing a large object–detector distance before the resolution will be compromised. The standard solution to overcome the problems associated with the zero-crossings in the CTF is to acquire each projection angle from the right-hand side of Eq. (2) to be replaced with a single unknown image \( I_0 \) and enables the phase-contrast model to be rewritten as follows:

\[ \hat{F}(I_R) = (\cos(\lambda R u^2) + 2 \alpha \sin(\lambda R u^2)) \cdot \hat{F}(I_0), \]  
(4)

where \( \alpha \) is a constant that depends on the composition of the specimen; it quantifies the ratio between attenuation and phase effects. Reconstruction based on Eq. (4) allows retrieval of an image of the specimen from a single recorded image \( I_R \). Unfortunately, similar to Eq. (2), it is impossible to reconstruct the image for spatial frequencies at which the right-hand side of the equation is zero. In order to overcome this limitation, a solution similar to Eq. (3) can be used. By combining Eqs. (3) and (4) we can reconstruct the image of a homogeneous specimen over a wide frequency range including the low frequencies. The resulting phase-attenuation formula can be written as:

\[ \hat{F}(I_0) = \sum_k A_k \hat{F}(I_k) \sum_k A_k, \quad A_k = (\cos(\lambda R u^2) + 2 \alpha \sin(\lambda R u^2)), \]  
(5)

Here the number of images that have to be recorded per projection angle can be selected depending on the desired frequency bandwidth of the reconstruction.

An alternative approach to mixed TIE-CTF phase retrieval was proposed in Ref. [10] for homogeneous specimens and subsequently modified in Refs. [11,12]. We refer to it as the phase-attenuation duality approach. The underlying assumption of this approach is that the phase image \( \phi \) is highly correlated with the attenuation image \( I_0 \). This allows two unknown images \( \phi \) and \( I_0 \) from the right-hand side of Eq. (2) to be replaced with a single unknown image \( I_0 \) and enables the phase-contrast regime. In fact, they produce such a high
considering the experimental technique that was used in the current investigation, it is only possible to reliably detect large cementite grains that occur after very long annealing times. Information on the interface mobility and preferred growth orientation of the large cementite grains can be obtained in a time-dependent PCT experiment (with a resolution of 1.5 μm). It is, however, desirable to develop a technique suitable for observations of smaller cementite grains that form after shorter annealing times and ultimately cementite grains during the nucleation process. We believe that the parameters of the current PCT acquisition protocol can be relatively easy adjusted in order improve the sensitivity of the method by a large factor. The most important experimental parameters in PCT are the energy of the X-ray beam, the object–detector distance, the resolution of the detector and the spatial coherency of the X-ray source. We expect that the resolution and the spatial coherency of the X-ray source can be improved by approximately a factor of 2 by adjusting parameters of the current experimental set-up. If the projected thickness of the specimen does not exceed 100 μm, the X-ray energy can be reduced from 40 down to 30 keV. Considering the properties of the propagation model (2) and the properties of materials, the magnitude of the observed phase-contrast effect is roughly inversely proportional to the third power of the X-ray energy. This means that the sensitivity of the method can be improved by a factor of 4 by decreasing the X-ray energy. Using the phase-attenuation duality approach it is possible to perform tomographic reconstructions from the PCT data recorded at a single object–detector distance. This should limit the acquisition time for a full tomographic dataset to less than 30 min at the ESRF or similar large-scale synchrotron radiation facility.

Based on the aforementioned analysis, we have shown that a state-of-the-art PCT approach is suitable for the detection of the cementite structures with sizes down to a few microns. We show that PCT can be used for the non-destructive study of the 3D morphology of individual cementite particles in steel with a spatial resolution of ~1.5 μm in a sample volume of at least 600 × 400 × 250 μm³. The PCT results correspond very well to optical microscopy in combination with serial sectioning. We demonstrate that PCT is suitable for the in situ study of the evolution of the morphology of the cementite of individual cementite particles in 3D during processing of steel with an estimated temporal resolution of 30 min. This allows in situ experiments aimed at investigating the cementite grain growth rates, the cementite morphology evolution and the mobility of the ferrite–cementite interface in steel at elevated temperatures.

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Figure 3. 3D rendering of the cementite structure in ferrite bulk. The total volume dimensions are 600 × 400 × 250 μm³. Rendering shows a highly interconnected network of cementite particles.

Figure 4. Rendering of a single interconnected cementite structure, where (b) is a cross-section made in the x–y plane in the middle of the grain, (c) shows the corresponding plane in the phase-contrast data and (d) is the corresponding optical image obtained from the serial sectioning of the specimen.