Ion beam tomography of the nano- and microstructure of cementitious materials

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ABSTRACT

Novel 3D-microscopy methods, including Focused Ion Beam – nano-tomography (FIB-nt) and Broad Ion Beam – tomography (BIB) have been applied to the characterisation of nano- and micro-cracks in cement based materials. FIB provides a nanometric resolution of the three-dimensional distribution of cracks and porosity, thus enabling a tomographic reconstruction of samples ranging from a few hundreds of nanometres to a few microns in thickness. On the other hand, the BIB tomography approach extends the scale of study until a few tens of microns. The application of these techniques to the study of cementitious materials has been quite limited until present. In this work, we report on preliminary results that show the feasibility to use FIB and BIB to map and quantify the parameters that play an important role in the modelling of water transport and, by extension, the prediction of the durability on the basis of the multiscale identification of microcracks, micro and nanoporosity, reaction products and detailed distribution of cement components.

Keywords: Focused Ion Beam (FIB), Broad Ion Beam (BIB), tomography, microstructure, micro-cracking, cement, concrete.

1. Introduction

Concrete is the most widely used building material in the world. It is a composite material, which consists of cement and other cementitious materials such as fly ash and slag, aggregate (generally a coarse aggregate made of gravel or crushed rocks and a fine aggregate such as sand), water, and chemical admixtures. The chemical bonding of individual components give a material with designed features of: strength, permeability and durability.

Durability of concrete can be described using the concept of service life, i.e.: “the time during which a concrete fulfills its performance requirements” [1], without non-intended maintenance. Durability depends not only on the original material composition and properties, but also on the environmental actions during service. Understanding transport process and getting knowledge on the microstructure of cementitious systems is the key point to predict the durability of cementitious materials, drawn out from service life and thereby reduce energy consumption in concrete manufacture.

In cement-based materials, porosity and cracks play a major role in transport processes. Recent experimental techniques for the characterisation of porosity and micro-cracks in mortar and concrete in 3D may provide important information about the effect of microstructure on mass transport, which is a critical aspect for predicting durability of concrete [1].

In materials science, various techniques for three-dimensional reconstruction of microstructures, such as X-ray tomography, focused ion beam microscopy and transmission electron microscopy, have been applied successfully [2]. All these methods have some advantages and disadvantages. The significant problem is the adequate balance between resolution and representativity of the objects of interest.

The micro-cracks are defined as cracks, which have a maximum width of less than 50µm [3]. For this, the resolution of the FIB-SEM technique is excellent. Unfortunately, the investigated volume of the sample is rather small (a few cubic microns) and therefore cannot be assumed to reflect a representative elementary volume. A multi-scale microscopy approach is required. In this work, we propose to analyse the "fine" elements of microstructure with Focused Ion Beam nano-tomography (FIB-nt) in a small specimen volume (μm^3 range) and the "coarse" elements of the microstructure with Broad Ion Beam cross-sectioning (BIB) in a "large" volume (mm^3 range).

2. Methods

2.1. FIB-nano tomography

The Focused Ion Beam (FIB) is a relatively new and powerful instrument, which combines imaging capabilities with a precision machining tool. Combination of a focused ion beam source and a scanning electron microscope SEM in one system allows both imaging and sample modification in situ [4].

One of the applications of this system is FIB nano-tomography (FIB-nt). It is a process, in which a region of interest (ROI) in a sample is FIB serial sectioned and SEM imaged after each successive single cross section. Three-dimensional reconstruction of the original object is obtained when the individual images are arranged in a proper order by the appropriate software [5]. This procedure includes a few steps, including: preparation of a cube of suitable size, application of reference marks on the top of the cube, serial sectioning and acquisition of a stack with hundreds of images with drift correction after each cycle of imaging and erosion, and off-line data processing (alignment of image stack, 3D reconstruction, segmentation, visualization, and quantification) [6, 7].

2.2. BIB cross sectioning

Broad Ion Beam (BIB) is used for ion etching, polishing, thinning, depth profiling and also for cutting [8]. BIB is an atomic scale erosion process mainly based on Argon source (typically in the range of 2-10 keV) to prepare 2D flat undamaged surfaces in the range of $2mm^2$, suitable for high resolution SEM imaging of sub-micrometric microstructures. The ion beam irradiates the edge of sample un-masked by the shielding plate to split the ion beam in order to create a vertical polished surface beneath the shielding plate. In comparison with FIB (Gallium source, 30 keV, typical cross-section of about 100-500 μm^2), BIB has two main advantages: (1) it is potentially less damaging since it is based on noble gas source and (2) it produces cross section area which fits better to the typical length scale range of microstructures and representative elementary area in cementitious materials [9, 10].

3. Materials

Cement paste (w/c = 0.4) and mortar (w/c = 0.5) with standard sand (aggregate <0,4mm) were produced using a CEM I 32,5 cement and distilled water. Fresh cement paste and mortar were casted $3x3x1.5cm^3$ specimens and demoulded after 4 hours. Samples were cured under high relatively humidity conditions (95±2%) for 4 days and then oven-dried at 30^oC for 3 days. After that, specimens of 10x10x5 mm^3 were prepared using a diamond saw. Subsequent hydration was stopped by solvent exchange methods. The samples were impregnated with a low viscosity epoxy resin. Impregnation was followed by grinding to remove surplus epoxy. Such a sub-samples were then prepared by using either a stand alone BIB cross sectioner

(JEOL-SM 09010) or a FIB embedded into the SEM to prepare high quality surface suitable for high resolution imaging in SEM. For both methods, the produced ion beam polished surfaces are coated with gold to minimize the charging effect under SEM.

4. Experiment

4.1. FIB nano-tomography

For the FIB-nt study, the sample was placed at the eucentric point, where the surface is perpendicular to the ion beam (Fig. 1-1). The optimal magnification, focusing, brightness and contrast were adjusted for a working distance of 5.2 mm. Then, region of interest was chosen and covered with a thick Pt layer (Fig.1-2.). Trenches were eroded with a FIB in front of and at both sides of the Pt layer. Additional the reference marks were done for the drift correction (Fig.1-3).

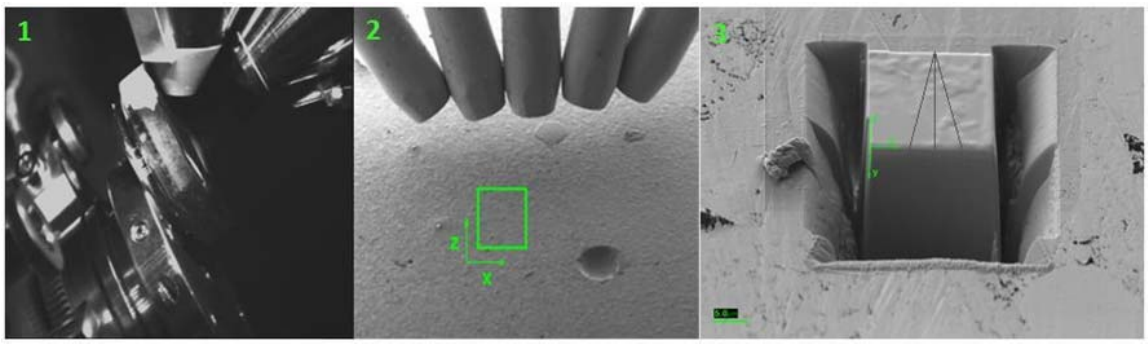

Fig. 1. Cube preparation for FIB-nt.

When the cube was ready, the serial sectioning procedure was started. This is a commutative procedure in which a thin layer of material from the x-y plane is eroded with the ion beam and the newly exposed surface is subsequently imaged by SEM. In this way, a stack with hundreds of images was produced (see Fig.2.), while moving through the sample in the z-direction. Processing time took between 8 and 12 hours, and the thicknesses of the layers were about 20-50 nm depending on the size of the cube.

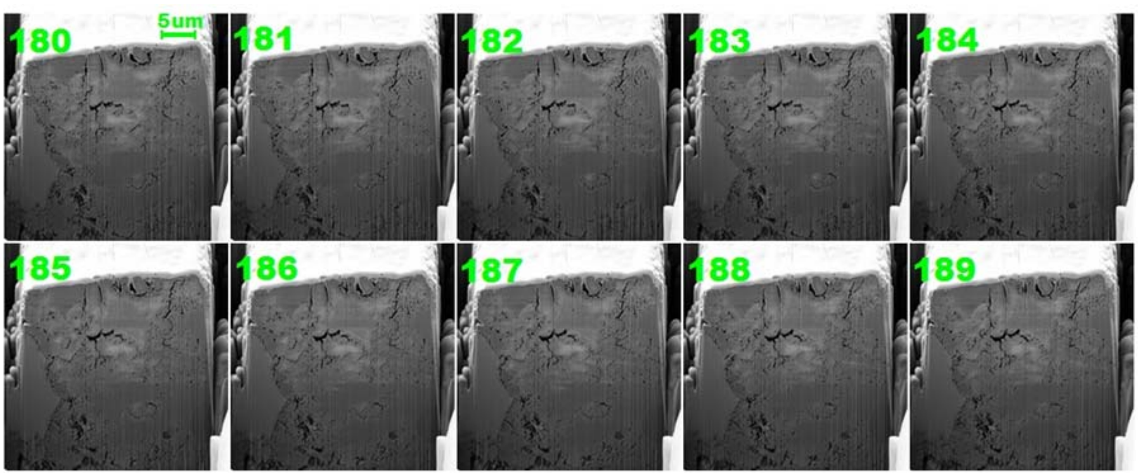

Fig. 2. Selection of 10 subsequent images (slices no. 180-189) from the raw data stack of mortar.

4.1. BIB-cross sectioning

The stand-alone BIB argon machine was used to perform a serial cross sectioning procedure in order to estimate the evolution of the microstructure in 3D. Five successive slices were produced under similar conditions (6keV, 8hrs); resulting polished surfaces were about 1mm^2. Each section was imaged with an SEM using a secondary electrons detector. A mosaic made of several dozen single images was carried out in order to produce an over view of the entire BIB cross-section. Then, within the BIB cross section, ROIs of about 200 x 300 μm^2 were selected in order to map them down to the resolution of SEM. These ROIs are mosaics made of hundreds of single images taken at high magnification (x 14,000) giving detailed insights into the porosity and μ-crack patterns. This procedure was repeated for all of successive cross-sections, which have been subsequently aligned to follow the evolution of microstructures with direction of serial-sectioning.

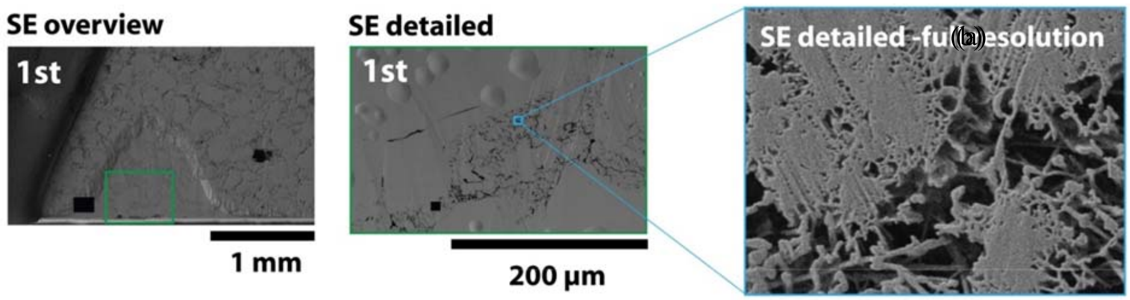

Fig. 3. Overview of first cross section, selected region, one element (picture) of mosaic.

5. Results

5.1. FIB nano-tomography

Image processing of performance stack of hundreds images and reconstruction in 3D was carried out with a Fiji 3D^{TM} reconstruction software (available online at: http://pacific.mpi-cbg.de/wiki/index.php/Fiji). The procedure includes:

1) Correction of voxel dimensions, alignment of image stack and overlay correction for x-y drift.

The total dimension in the x-direction was obtained from a calibrated FIB magnification scale. Then the distance in the y-direction was corrected for projection effect using $y' = y \times \sin\alpha$ (α=54º). For each layer, z-values were obtained from the measured cube thickness of the stack divided by the number of slices.

2) Crop-out of a suitable subvolume (Fig.4-1.). For the analysed cube, a representative subvolume was defined.

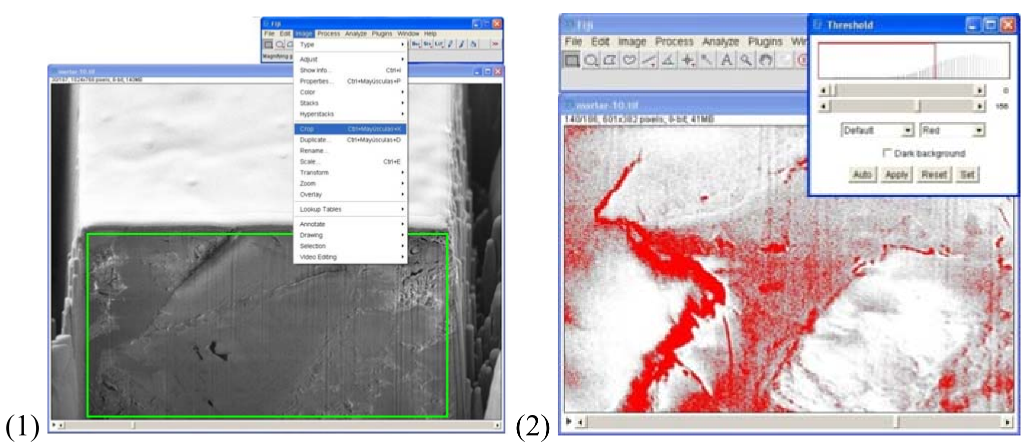

Fig. 4. Crop-out of subvolume (1) and segmentation (2).

3) Segmentation, binarization and visualization. The dark phase (cracks and porosity) was selected from the grey scale. The selected phase appears in black and the rest in white. Then several procedures were adjusted to improve the selection, including noise reduction, particle size filtering, erosion, and dilation. These processes were necessary, because phase selection is based on the grey level of the pixel (Fig. 4-2). Three dimensional reconstructions are shown in Fig. 5.

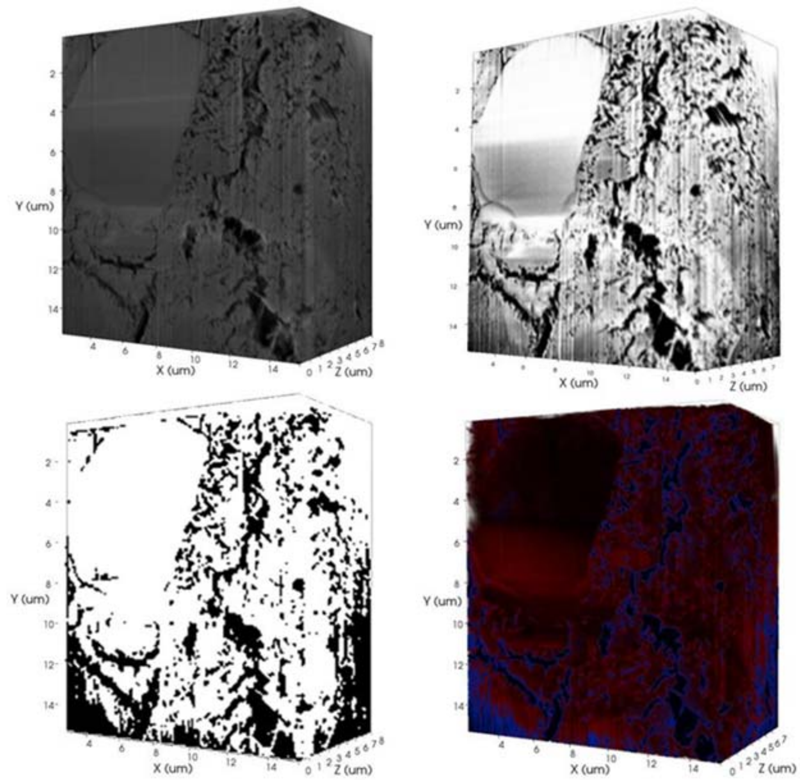

Fig. 5. 3D reconstruction of cement paste: raw data after preprocessing (two top), after segmentation (bottom left), after segregation objects (bottom right).

5.2. BIB-cross sectioning

Hundreds of single images from each cross section were stitched together by using Autopano^{TM} software to produce high resolution mosaic images (Fig. 6).

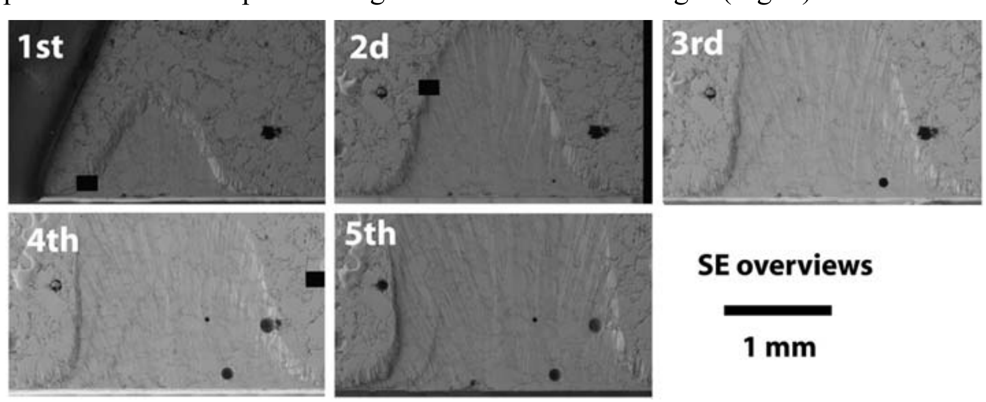

Fig. 6. Five successive cross-sections imaged with secondary electrons.

During the experiment the slice thickness was adjusted to 15 µm. The reconstructed mosaic of each cross section was aligned in 3D using ArcMap™ 9.3 software. For segmentation and quantification of the microstructures, Fiji 3D™ reconstruction software was also used. The black phase (micro-cracks, voids and porosity) was thus distinguished from the solid (white phase) (Fig.7.).

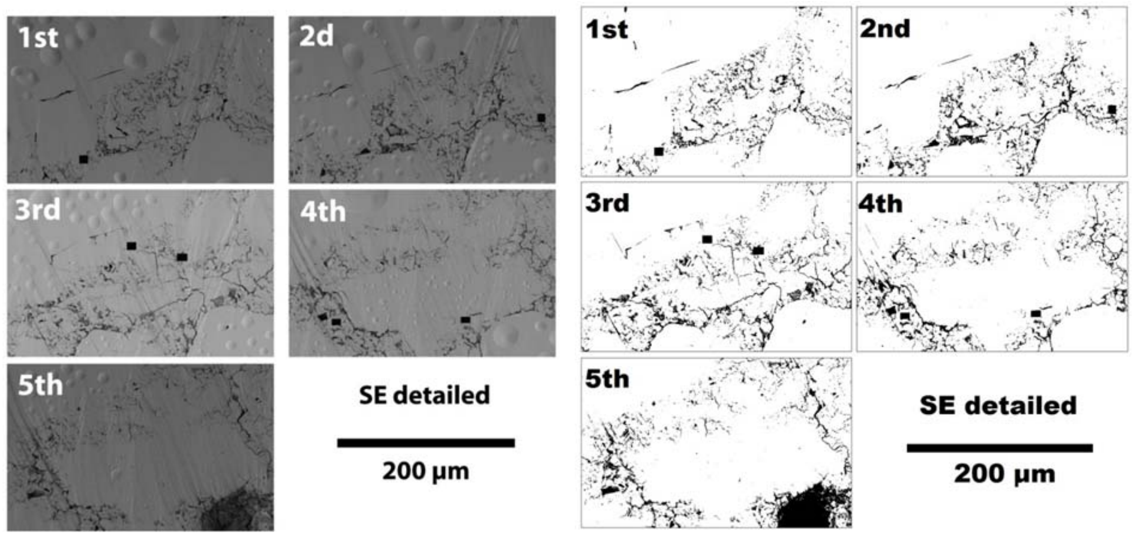

Fig.7. Data processing: images after stitching (grey scale) and after segmentation (black and white scale).

4. Conclusions

FIB-nt is a novel high resolution method, which can bring 3D data that are suitable for quantitative microstructure analysis of cementitious materials.

Serial cross sectioning also allows investigation of the evolution of the microstructure in 3D, but in a larger scale. Three-dimensional information about micro-cracking can thus be obtained and quantified using a combination of FIB-nt, and BIB cross-sectioning. The integration of 3D data from two methods into a consistent micro-structural model will require extensive experimental and computational analyses.

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