Using nano-indentation and microscopy to obtain mechanical properties

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Abstract

Simulation of mechanical behaviour of heterogeneous materials is only possible if the local properties of the components are known. In recent years nano-indentation is being applied on different levels to obtain local mechanical properties. The aim of this paper is to explore various ways to obtain these properties by combining nano-indentation and microscopy. The method to prepare specimens and perform the testing is explained and the way the properties are used in the modelling is discussed.

Keywords: nano-indentation, hardness, stiffness, lattice model, multi-scale modelling

I. Introduction

Multi-scale modelling is a popular technique to get insight into mechanical properties and to explain damage and deterioration mechanisms in cement based materials. With a model on a certain scale the (non-linear) properties of a material on that scale can be predicted. These properties can subsequently be used as input parameters for the local properties on a next scale as sketched in Figure 1. Here the microstructure of a cement paste is simulated using the HYMOSTRUC 3D model (Figure 1a) according to Ye (2003). This microstructure can then be used to study the mechanical properties of a cement-paste cube at a certain degree of hydration (Qian et al. 2011). For the simulation of the fracture behaviour various types of models can be used, such as discrete element type or lattice type models (Schlangen, 1993). The outcome of such a simulation on the scale of cement paste is a non-linear stress-strain relation which can be used as input for the simulation of mechanical properties of mortar as depicted in Figure 1b. The outcome of a simulation on the mortar scale is again the input for the concrete scale in which the aggregate particles in the material, see Figure 1c, should be modelled (Qian, 2012).

To be able to perform simulations of a heterogeneous material on a certain scale the local properties of the components of the material have to be known. For instance, for simulating the mechanical behaviour of the cement-paste shown in Figure 1a, the mechanical properties of the single phases (unhydrated cement and different hydration products) are required. For the simulation of the concrete in Figure 1c the properties of the aggregates and the mortar are needed as well as the interface between them. These local properties are not easily measured. Various attempts can be found in literature to obtain them from direct tests on for instance an aggregate attached to a cement paste (Ağar-Özbek et al, 2013) or trying to simulate them with a lower scale model (Bentz et al. 1995). Furthermore it should be noted that these local material properties, such as strength and Young's modulus, are most probably not single values, but the local behaviour is actually a non-linear stress strain relation. At the atomic scale the local mechanical behaviour might be brittle, but at all higher scales some non-linearity has to be implemented in the multi-scale modelling concept. This non-linearity is different at each scale, which makes it rather complex. The general procedure to simulate mechanical response is to start with a brittle behaviour for fracture at the lowest scale of observation (see e.g. Qian, 2012) and then use non-linear behaviour at all higher scales to keep the error as small as possible.

Another way to obtain local mechanical properties that can be used as input for simulations is nano-indentation. This method is initially developed for homogeneous materials and especially thin films to obtain local mechanical properties such as hardness and stiffness. However it is also used to get local mechanical properties of heterogeneous materials by indenting in the different phases of the material. First applications for cement-based mate-

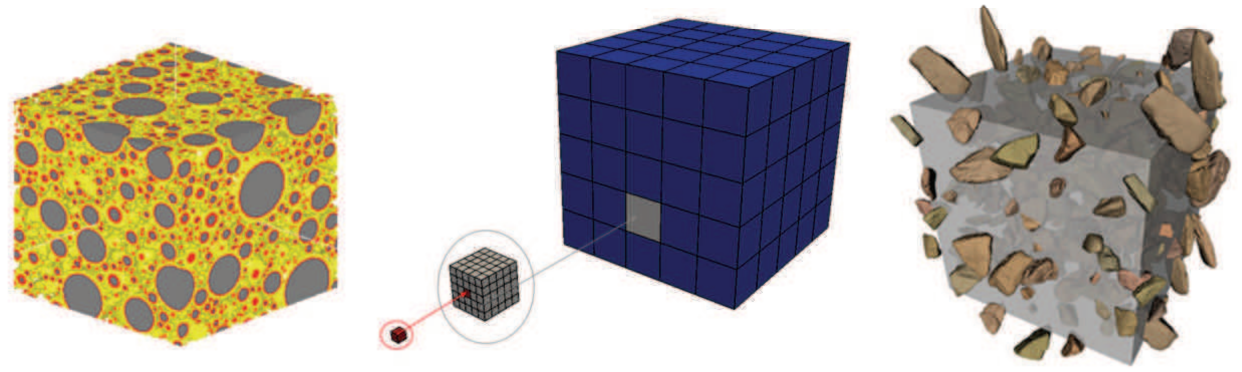

Figure 1: a) Generated cement-paste microstructure, b) multi-scale modelling scheme and c) generated concrete sample with irregular aggregates.

rials can be found in Constantinides and Ulm (2004) or Hughes and Trtik (2004). Using these properties as input for modelling mechanical properties of cement paste material is shown in Bernard et al. (2003) and it is applied for simulating degradation mechanisms by Çopuroğlu and Schlangen (2008).

The difficulty with nano-indentation in heterogeneous materials is that it is impossible to indent in a single phase and the materials are generally 3D, which means the material below the indent might be of a different phase. The results obtained from the indentation will therefore always be a combined property of various phases. Furthermore the properties from nano-indentation cannot be directly implemented into a model. Local properties of an element in a model might be dependent on the scale of the element or other parameters that are specific for the model that is used.

The aim of the study presented in this paper to give more insight in the use of different nano-indentation techniques for cement-based materials at different scales and the way the outcome from the nano-indentation measurements can be used in models.

In this paper three different ways of applying nano-indentation to obtain mechanical properties are discussed. All methods are supported by numerical simulations with a lattice model. The first method is used to obtain local properties in a repair system of repair material (cement paste) on a mortar. Main focus is on the properties of the zone around the interface and whether the local mechanical properties can be linked to the failure of the interface. The second method is a 3D nano-indention on cement paste samples to study the effect of the sub-surface microstructure on the measured properties. Finally the use of nano-indentation to obtain more global properties of cement paste is presented.

II. EXPERIMENTAL PROCEDURE AND RESULTS

Specimen preparation

The specimens used in the three methods of nano-indentations are all prepared in the same way. The specimens were prepared for a study on the performance of repair systems (Luković, in preparation). The substrate was 5 year old mortar casted with Ordinary Portland Cement (OPC) CEM I 42,5 N. Smaller mortar specimens were cut with a diamond saw from bigger samples and fixed in the centre of

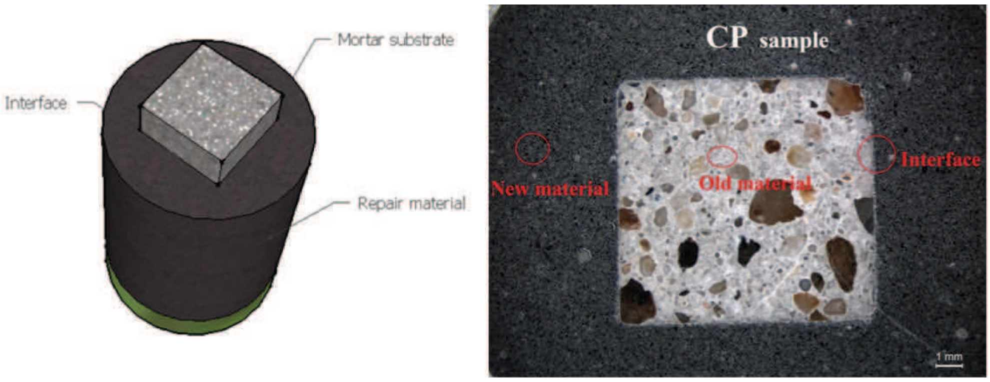

Figure 2: a) Mortar-cement paste cylindrical sample to study local mechanical properties and b) zoom-in on interface between mortar and cement paste.

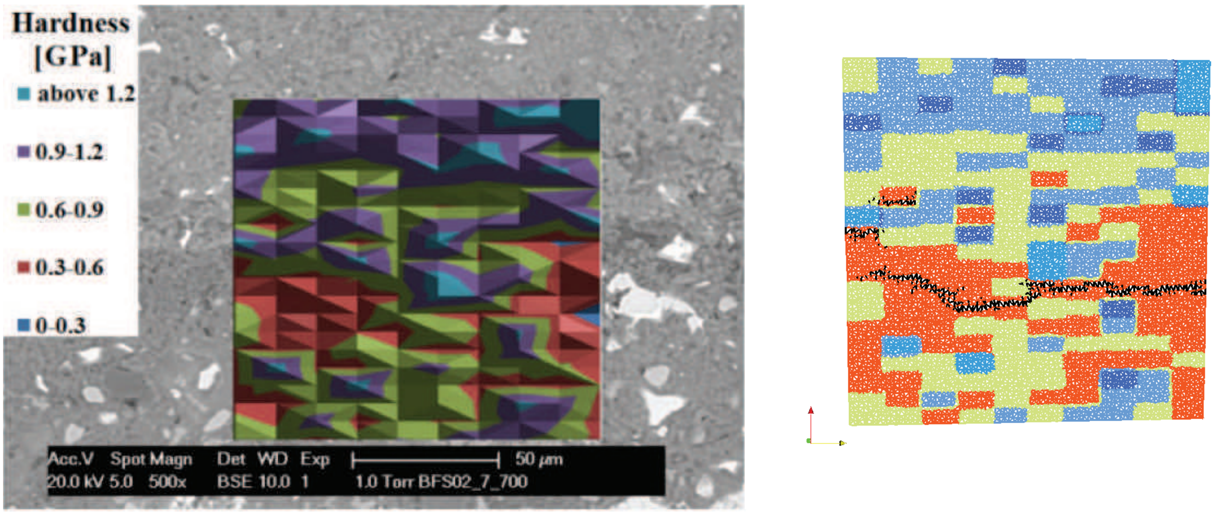

Figure 3: a) Nano-indentation measurements of hardness projected on top of ESEM image of microstructure in the interface region and b) simulated result of tensile test with implemented local properties from nano-indentation measurements.

the mould where new material was later cast (Figure 2). Before casting it, the old mortar was placed for 24h in a chamber with 80% relative humidity, in order to enable hygral equilibrium and uniform moisture profile in the substrate. The repair material (cement paste) was a standard grade OPC CEM I 42,5 N paste with 0.4 water-to-cement ratio. Cylindrical specimens (diameter, 24 mm, height 39 mm) were cast. The specimens were cured for 28 days in sealed conditions at room temperature of 20°C. After 28 days, the sample was cut with a diamond saw into slices with a thickness of 8 mm. In order to stop hydration, solvent exchange by isopropanol was used. The sample was submerged five times and taken out for a period of one minute in order to enable faster water-solvent exchange. Afterwards, it was placed for 72 hours in isopropanol and subsequently taken out, and solvent was removed by evaporation at ambient conditions. In order to make thickness of the specimens even and uniform, a thin sectioning machine was used for cutting and grinding of the specimen. An object glass was glued on the sample and a block was cut with a diamond saw (Figure 3). Afterwards, all samples were ground in the thin section machine in several passes. After grinding, each of the samples was polished with 6 μm (5 min), 3 μm (5 min), 1 μm (5 min) and 0.25 μm (25 min) diamond paste on a lapping table. After every step, an optical microscope was used to check the effectiveness of grinding and polishing. Finally, the samples were soaked into an ultrasonic bath to remove any residue from the surface. Samples were kept in a desiccator under vacuum until testing.

2D nano-indentation

Agilent Nano Indenter G200 with a diamond Berkovich tip was used for nano-indentation tests on the samples in order to measure the local mechanical properties around the interface between mortar and repair material. More details on these tests are described in Luković et al. (2014). A series of indents were performed on a tightly spaced grid, with spacing of 7 μm in the direction perpendicular to the interface, and 14 μm in the direction parallel to the interface. The indentation depth was 700 nm. The Continuous Stiffness Method (CSM) developed by Oliver and Pharr (2004) is used. This method consists of superimposing a small oscillation on the primary loading signal and analysing the response of the system by means of a frequency-specific amplifier. As a consequence, it enables a continuous measure of contact stiffness as a function of indentation depth and not just at the point of initial unloading. Therefore, hardness and elastic modulus are obtained as a continuous function of surface penetration. The average E-modulus and hardness were determined in the displacement range between 500 and 650 nm depths. The indentation areas were taken randomly within the interface between the old mortar and new cement paste.

After nano-indentation testing, samples were examined using environmental scanning microscope (ESEM), in backscattered electron (BSE) mode. The instrument was operated at 20 kV accelerating voltage and at 10 mm working distance between the final condenser lens and the specimen. The spot size was 5.0 μm and the magnification was 500×. The vapour pressure inside the chamber was set to 1 Torr. All imaging was performed at low vacuum in order to reduce the probability of cracking in

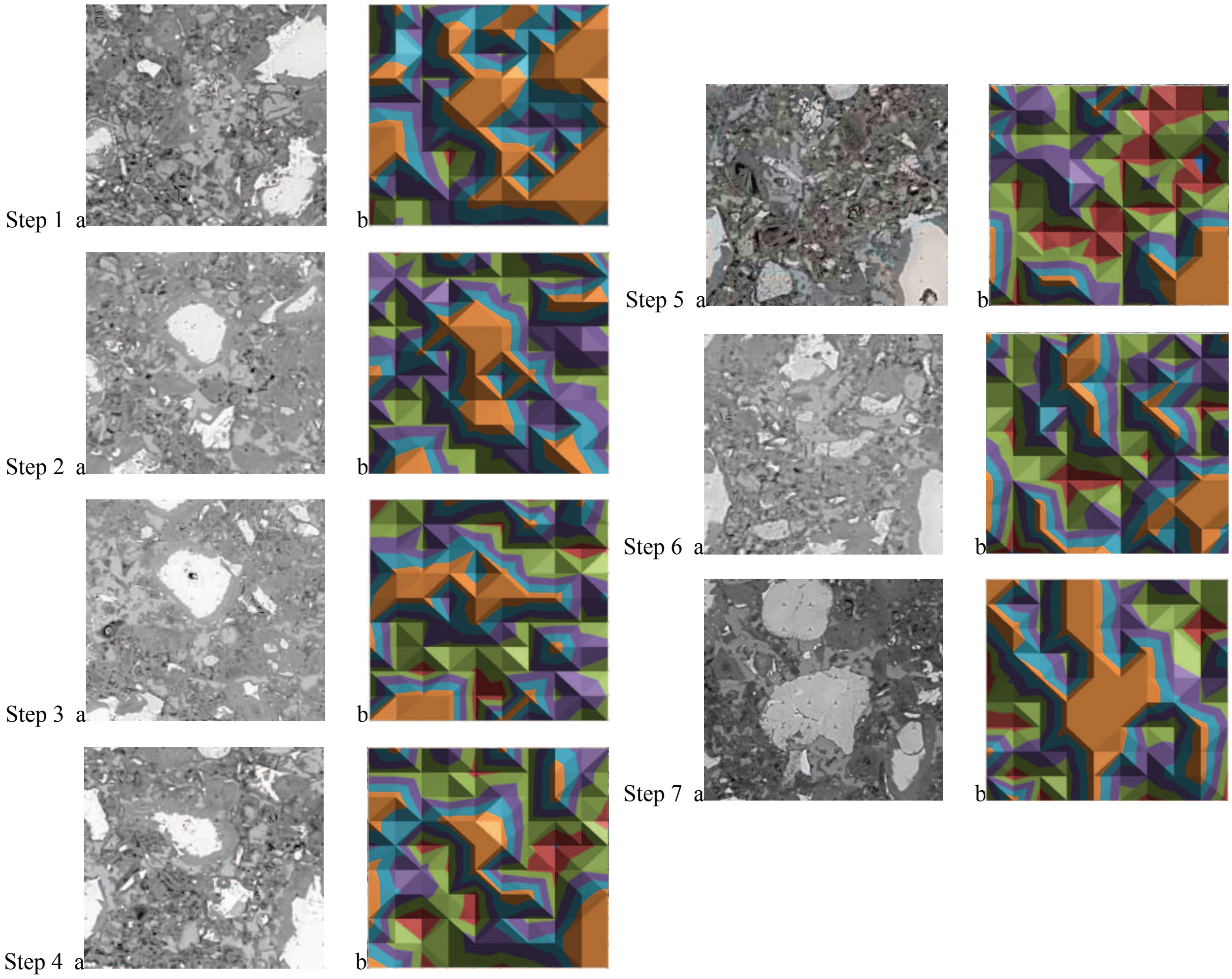

Figure 4: a) ESEM-images (100x100 µm) of tested locations and b) measured hardness values with nano-indenter.

the specimens. The nano-indentation hardness is plotted in Figure 3a on top of the microstructure that is obtained using ESEM. It can be seen that the very heterogeneous structure of the interface on microscale contributes to high variations and a not so clear tendency around the interface. Also, these local micromechanical interface properties do not provide any information about the interface performance and its strength. Therefore, they need to be linked together in a structure where all the single local tests will be assembled. This will enable assessment of the overall performance of the interface zone and estimation of the fracture properties at the micro-scale. This is done by combining the experimental results with numerical simulations. Measured local micromechanical properties are used as input for numerical modelling with the lattice model which enables estimation of the global micromechanical response (properties) of the tested microstructure. An example of this is shown in Figure 3b, where a 2D sample is loaded in tension (vertically). The local properties implemented in the model correspond with the local hardness and stiffness as measured in a sample shown in Figure 3a. The final crack pattern that is the outcome of the simulation is shown by the black line in Figure 3b. More results and comparison of experimental findings and simulated results can be found in Luković et al. (2014).

3D nano-indentation

Nano-indentation gives local mechanical properties for the surface of a material. For heterogeneous materials this always results in an error since the phase of the material below the surface might (and will) be different in most cases. The effect of evaluating 2D instead of 3D quantities is examined by a combination of experimental and numerical research (Luković et al., 2015). In this study, nano-indentation testing was applied on successive slices in cement paste. The same specimens and preparation method as explained above were used. First, one slice was prepared, tested in nano-indentation and checked in ESEM (Environmental Scanning Electron Microscope). Then, the top layer (around 16 μm) is removed, the sample polished, and the same area tested again. A procedure, ensuring that the same area is tested in every consecutive slice, is developed. After nano-indentation testing of con-

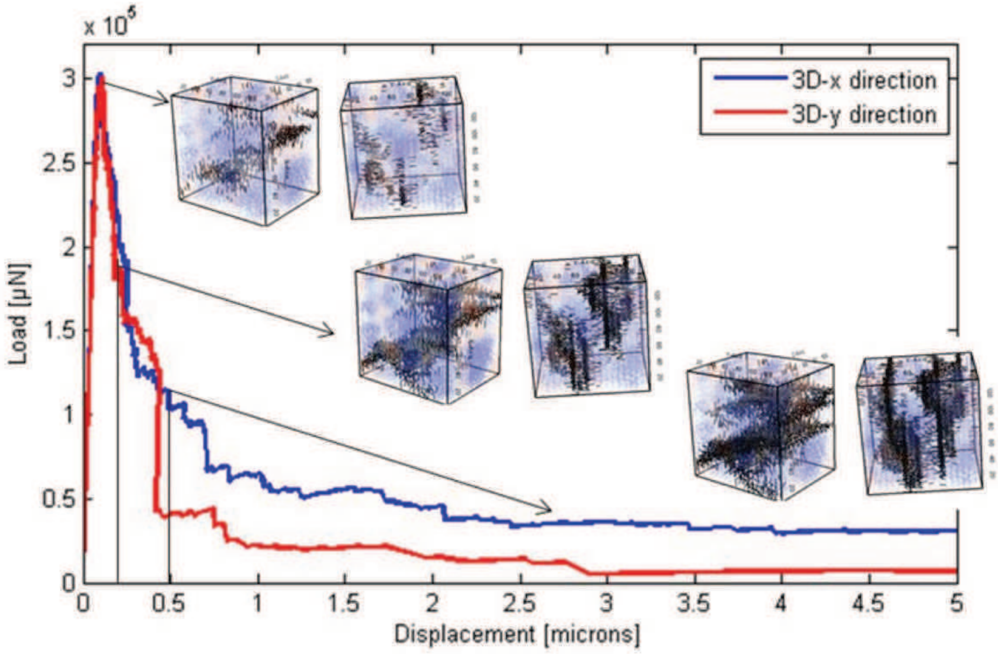

Figure 5: Simulated tensile test on 3D cube with loading in x and y direction and local properties from nano-indentation measurements.

secutive layers, all individual 2D microstructures and a reconstructed 3D microstructure (obtained by reconstruction of individual 2D slices) were subjected to simulated direct tension testing.

In Figure 4a, only part of microstructure where the indentation testing was performed with corresponding hardness properties (Figure 4b) are presented. From ESEM image in Step 1, it seems that in the middle of the tested specimen only CH and CSH are present. However, nano-indentation results indicate much higher hardness properties than those corresponding only to CH and CSH phase. From ESEM image in Step 2, it can be observed that exactly under this first layer, there are two unhydrated cement particles, which contributed to locally higher micromechanical properties that are observed in Step 1. Similar observations are made also in some of the further steps. Nano-indentation results at some locations, therefore, can be explained only if the following step is analysed. It should be kept in mind that nano-indentation is, after all, volume testing, and results cannot be always directly related to the phases observed on the surface. This holds especially for highly heterogeneous materials such as cement paste.

As can be seen from Figure 4, cement particles are very irregular and randomly distributed. Their alignment, distribution and mutual interaction would highly influence both on microstructure development and on fracture properties.

Figure 5 shows an example of a simulation with the lattice model of a small cube loaded in tension. The properties use as input are obtained from the 3D nano-indentation. The cube is loaded in 2 directions and the resulting load-displacement curves and crack patterns are compared. The scatter in load-displacement curves is small when the 3D input data are used and a 3D simulation is performed. This is, however, different when only 2D input data from different slices are used as discussed in Luković et.al 2015. This results in bigger scatter.

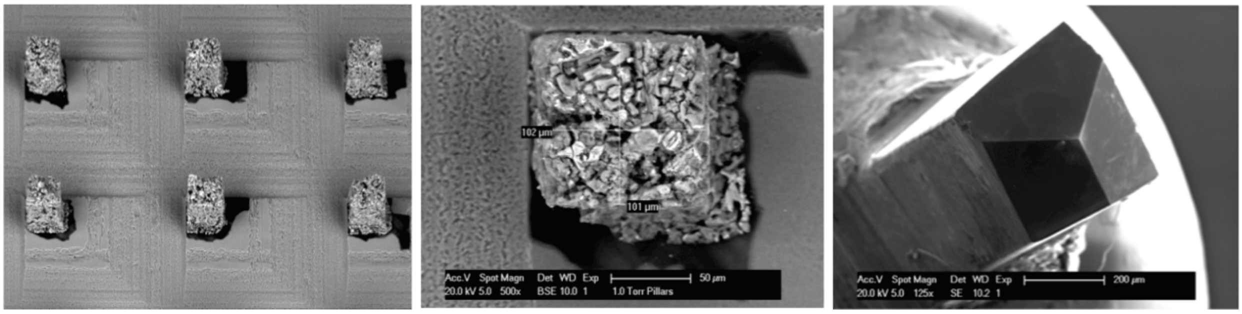

Figure 6: a) Small cement paste cubes on glass plate b) Single cube with dimensions c) Diamond Berkovich tip.

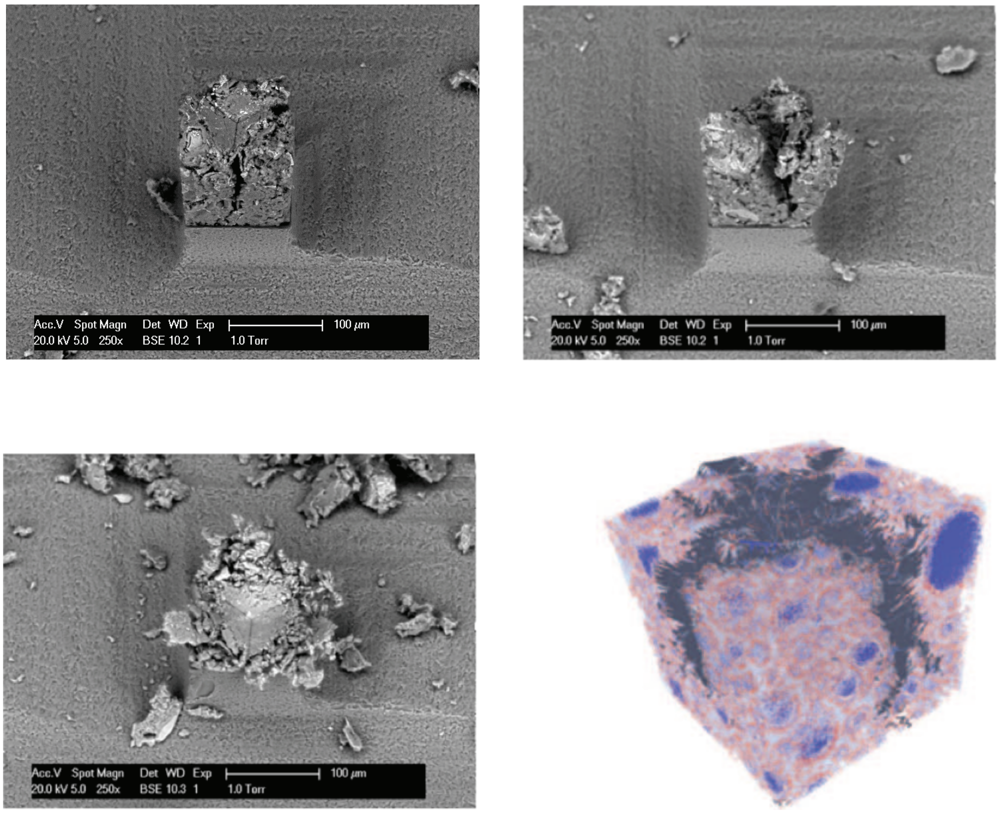

Figure 7: Three stages (a, b, c) in the nano-indentation loading process of small cubes observed in ESEM and simulation result with the lattice model (d).

Nano-indentation of small cubes

As discussed before, nano-indentation in a heterogeneous material as cement paste never results in properties of a single phase. Properties that are found by nano-indentation can be implemented into models, yet an error will be made. When using upscaling methods it is therefore necessary to check and validate the effect of the choice of your input values for your model on every scale. This should be done with experiments and not by modelling because then the errors might only pile up. In (Schlangen et al. 2015), a new method is proposed to study the failure of 100 μm cement paste cubes under indentation loading. The same basic specimens as described above were used. In order to make the thickness of the specimens equal to 100 μm and even and uniform, a thin sectioning machine was used for cutting and grinding of the specimen. Next step in the process is to create small cubes from the 100 μm thin slice. For this process a diamond dicing saw for semiconductor wafers was used. By running this precise saw with a 400 μm wide blade in two directions over the thin section small cubes as shown in Figure 6a were obtained. To prevent chipping of the edges of the small cement paste cubes while cutting, a thin layer of nail-polish was applied on the surface of the thin section, which was later removed by soaking the specimen for a short time in acetone. The dicing saw machine was set in such a way that the saw was cutting a few micrometres into the glass plate in order to make sure that the cement paste cubes have the required dimensions and that also the glue between cement paste and glass was sliced. The final cubes are all at the dimension of 100x100x100 $\pm$ 3 μm (Figure 6b).

The small cubical cement paste samples on the glass plate were placed in an Agilent G200 nano-indenter and were tested with a Berkovich tip (Figure 6c). A displacement controlled test was performed by using the CSM (Continuous Stiffness Method). The loading procedure is discussed in more detail in Poelma et al (2014) in which carbon nano tube bundles are loaded to failure with a nano-indenter. Different loading depths were applied. This made it possible to obtain crack patterns at various depths as shown in Figure 7. The typical failure mechanism obtained is crushing of the material under the tip and three main cracks running to the sides of the cubes, starting from the three edges of the Berkovich tip. Indenting the tip further into the specimen results in complete crushing of the sample as can be seen in the ESEM image in Figure 6c.

For the modelling a 3D lattice network model is used. As starting point for the simulations a 3 dimensional hydrated cement paste specimen is constructed using the HYMOSTRUC3D model. More details on the construction of these 100 μm cubes and the implementation of local material properties, obtained from local nano-indentation testing, can be found in Qian et al. (2011). The result of one of the simulations is presented in Figure 7d as deformed and cracked specimen.

III. Discussion and Conclusions

In this paper a combination of experimental techniques using nano-indentation and a modelling technique using 3D discrete lattice model simulations is applied to study the failure mechanism in cement paste specimens at micro-scale.

As input for the simulations, mechanical properties for the local lattice elements are needed. These can be obtained from local nano-indentation measurements in single phases of the heterogeneous composite. However, these properties cannot be used directly, because they depend on the size of the elements used in the model and should be transferred to model-parameters. Furthermore it should be noted that the results obtained from nano-indentation on the surface of a heterogeneous cement paste always includes an error, because the result is influenced by the phase below the surface.

In this paper different techniques and applications of nano-indentation are presented and discussed. First 2D nano-indentation is used to determine local properties around an interface between mortar and repair material. This method is valuable when studying for instance the influence of microstructure formation in a repair system and the resulting local mechanical properties on the performance and crack formation in such a system. A 3D nano-indentation method is shown which is useful to evaluate the influence and scatter of using 2D-data for studying 3D mechanisms. Finally a method is presented for making small scale cement-paste specimens and fail them with nano-indentation. This method is useful to validate experimentally simulation tools that are used in a multi-scale framework.

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