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Statistical nanoindentation technique in application to hardened cement pastes: Influences of material microstructure and analysis method

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HIGHLIGHTS

- The nature of indented microstructure is revealed.
- The influence of analysis method is comprehensively studied.
- A method for the verification of analysis result is proposed.

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ABSTRACT

Statistical nanoindentation technique has been widely used to study the microstructural mechanical properties of various types of hardened cement pastes, which has significantly improved the fundamental understanding on the mechanical performances of concrete and other cementitious composites. However, it was noted that the contradictory results from statistical nanoindentation technique appeared in the literatures and the critical aspects in the application of this technique to hardened cement pastes were recognized. This work is designed to provide an insight into the critical aspects, including the influences of material microstructure and statistical analysis method. Firstly, the microstructure of hardened cement pastes was investigated by SEM-BSE/EDX analysis. Then, the influence of heterogeneous material microstructure on the nanoindentation results was investigated through a micromechanical method. After that, two general methods of parameter estimation were applied to analyze the nanoindentation data and global optimal results were sought by multiple runs with the random starting values. This work revealed that the indented 'Calcium-Silicate-Hydrate' microstructure is a fact of the composites and the analysis result largely depends on the selected statistical analysis method. The influences of material microstructure and statistical analysis method may cause unreliable result. In this paper, a method for the verification of the result from statistical nanoindentation technique in hardened cement pastes was proposed.

1. Introduction

The mechanical properties of cement-based materials such as strength, ductility, creep, shrinkage, and fracture behavior largely depend on the material structure at the nano- and micro-scales. As an effective and powerful tool to detect the elastic properties and hardness of the local material microstructure, nanoindentation has been widely used to study the microstructural mechanical properties of cement-based materials (See [1] for a comprehensive review). To make the application of nanoindentation technique more convenient in interpreting the mechanical properties of complex microstructures of cement-based materials, statistical nanoindentation technique (SNT) was proposed to deconvolute the mechanical parameters of individual phases from a large array of nanoindentation tests on the polished surface of cement-based materials [2]. In SNT, statistical analysis exhibits noticeable advantages in the study of cement-based materials, e.g. researchers do not have to exactly know the location or material phase of each nanoindentation test. Therefore, statistical nanoindentation technique has been widely used in the study of microstructural mechanical properties of various types of hardened cement pastes at different water to cement ratios [3–14]. The identified phases

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from SNT on hardened cement pastes in term of indentation modulus and hardness from low to high were considered as LD (low density) C-S-H (Calcium silicate hydrate), HD (high density) C-S-H, UHD (ultra high density) phase and anhydrous [2,12,14]. In hardened cement pastes at low water to cement ratio, UHD phase was found to be a composite of HD C-S-H and nano-CH (calcium hydroxide) by coupled nanoindentation/SEM (scanning electron microscope)-EDX (energy-dispersive X-ray spectroscopy) analysis [15]. While, in hardened cement pastes at high water to cement ratio, the third phase is more likely to be CH rather than UHD phase, as indicated in some other works [4,6].

The critical aspects on the application of this technique to study the microstructure of hardened cement paste were recognized, consisting of the following two aspects:

a) One is the influence of the material microstructures, e.g. Trtik et al. [16] pointed out that the size of the interaction volume of nanoindentation is larger than the size of the single C-S-H phase, and the region scales of the homogeneous phases are too small to construct independent peaks in the PDF (probability density function) for the indentation modulus.
b) The other is the influence of statistical analysis method, e.g. the numerical instability in curve fitting was found in the work of Lura et al. [17] when trying to fit the experimental PDF of the indentation modulus using multiple Gaussian functions.

As statistical nanoindentation technique is an important and widely used technique in studying cement-based materials, this study is designed to study the influence of material microstructure and statistical analysis method on the nanoindentation results, and to provide an insight into the future application of statistical nanoindentation technique to cement-based materials.

2. Materials and experiments

2.1. Specimens preparation

To fulfill the aim of this work, necessary experiments were carried out on two cement pastes prepared at the same water to cement mass ratio (w/c) of 0.4, one is an ordinary cement paste (denoted as CP0.4) and the other is a blended cement paste with 10% (in mass) replacement of cement by silica fume (denoted as CP0.4SF). Firstly, the raw materials were mechanically mixed with deionized water and cast into steel moulds. After 24 h, the specimens were demoulded and cured in moist conditions (23 ± 1 °C and 95% relative humidity) to the age of 90 days.

Before the nanoindentation tests, the samples were carefully polished to achieve a smooth surface. The polishing procedure adopted in this study was used previously [18–21], and was divided into coarse polishing process and fine polishing process. Firstly, the samples were cut out from the middle portion of the specimens. Then, in the coarse polishing process, they were polished carefully with abrasive paper (180, 240, 400, 600, 800 and 1200 grit) in order. Each paper was used for 5–10 min. During the coarse polishing process, instead of water, an oil-based polishing fluid was used to prevent further hydration of the residual cement clinkers. After the coarse polishing process, oil-based diamond suspensions (3, 1, and 0.25 μm) were used in the fine polishing process. Each suspension was used for at least 30 min. During the whole polishing process, the pressure applied on the samples was only from the weights of the sample and the holder, and no extra pressure was applied on the samples. At the end of each step, a microscope was used to check the smoothness of the polishing. After being polished, the samples were cleaned in an ultrasonic bath with alcohol absolute to remove debris and suspensions left on the surfaces of the samples. The samples were then stored in a vacuum chamber for around 24 h before the nanoindentation tests. By using such a polishing procedure, the surfaces were smooth enough for the nanoindentation tests, as indicated in Fig. 1, where the nanoindentation footprints were observed by SEM and AFM.

2.2. Testing methods

In this study, all nanoindentation tests were conducted in ambient condition (typically 23 °C, 50% relative humidity). Fig. 2 shows a typical load-depth curve of C-S-H phase which was generated from the loading history with an initial constantly increasing loading, followed by constant holding and then constantly decreasing unloading. From the initial slope of the elastic unloading stage in the load-depth curve, two mechanical parameters can be simultaneously obtained [22], i.e. the indentation modulus, M, and the hardness, H, as defined below:

$$M = \frac{1}{2}\left(\frac{dp}{dh}\sqrt{\frac{\pi}{A}}\right)\Big|_{h=h_{\max}} \tag{1}$$

$$H = \left(\frac{p}{A}\right)\Big|_{h=h_{\max}} \tag{2}$$

where p is the indentation load, h is the indentation depth and $h_{\max}$ is the maximum indentation depth. A is the projected contact area and can be extrapolated from the indentation depth h through Oliver and Pharr's method [23]. For a homogeneous isotropic elastic material, the indentation modulus is related to the elastic modulus, E, and Poisson's ratio, ν, of the local material through [24]:

$$\frac{1}{M} = \frac{1-\nu^2}{E} + \frac{1-\nu_{tip}^2}{E_{tip}} \tag{3}$$

where E_{tip} is the elastic modulus of the indenter tip, and ν_{tip} is Poisson's ratio of the indenter tip. For the diamond tip used in this study, E_{tip} and ν_{tip} have values 1141 GPa and 0.07, respectively. The hardness is related to the yield strength of the local material, for example, for rigid cohesive plastic solids, Tabor suggests that the hardness to yield strength ratio equals 3 [25].

A Triboindenter equipped with Berkovich tip was used for the nanoindentation tests. The Triboindenter was calibrated on a standard sample (fused quartz). After calibration, one thousand nanoindentation tests were performed on each sample. Following that used in previous works [2,12,14], the maximum load used in this study was 2 mN, thus generating a maximum depth between 200 and 400 nm for the hydration phases. The results from the nanoindentation tests were decided by the mechanical properties of the local material microstructure, generally with the length scale around 3–5$h_{\max}$ [26]. Before the analysis of nanoindentation data, following the previous studies [27], the data stemming from the irregular nanoindentation curves shown in Fig. 3 were eliminated. For instance, Fig. 3(a) shows a flat region at the beginning of load-depth curve, which was caused by instable contact between the tip and the material surface at the initial loading process, that was a type of irregular appearance. Fig. 3(b) shows another irregular appearance, a shoulder appearance (sudden jump or pop-in due to the fracture and collapse of surrounding solids) on the load-depth curve. Generally, the data produced by such irregular curves do not belong to any materials phases. Thus the irregular curves were not used in statistical analysis. Totally, for CP0.4, 78 out of 1000 were rejected; for CP0.4SF, 35 out of 1000 were rejected.

To study the microstructural physical properties of hardened cement pastes, the samples were coated with carbon and then