46th International Scientific Conference EXPERIMENTAL STRESS ANALYSIS 2008
Department of Mechanics of Materials, VŠB - Technical University of Ostrava
June 2 - 5 2008, Horní Bečva, Czech Republic

Jiří NĚMEČEK*, Zdeněk BITTNAR**

NANOINDENTATION OF CEMENT PASTE

NANOINDENTACE CEMENTOVÉ PASTY

Abstract

This paper deals with nanoindentation of cement paste and the assessment of its local micromechanical properties. The contribution shows the complexity of cement microstructure and concerns on different approaches used for investigation of such heterogeneous material at submicron length scale. Three approaches were tested and results from nanoindentation and also ESEM were compared. Intrinsic material properties were assessed for high density C-S-H phase. Grid indentation with small or large indents and statistical evaluation was used in other cases. Moreover, indentation creep (short-term) was measured during the holding periods in the nanoindentation process.

Abstrakt

Článek pojednává o nanoindentaci na cementové pastě a stanovení jejich lokálních mikromechanických vlastností. Příspěvek ukazuje komplexnost cementové mikrostruktury a zabývá se různými postupy pro výzkum takovéhoto heterogenního materiálu na podmikrónové úrovni. Byly testovány tři přístupy a porovnány výsledky z nanoindentace a ESEM. Stanoveny byly vlastnosti pro high-density C-S-H. Indentace ve formě matice malých nebo velkých indentů a jejich statistické vyhodnocení bylo použito pro ostatní případy. Navíc bylo změřeno indentační (krátkodobé) dotvarování během fáze držení zatížení.

1 INTRODUCTION

Cement is the widespread building material whose impact to the environment is enormous. The overall behavior of any material is directly dependent on the microstructure and its individual phase properties. Modern constitutive models for composite materials try to respect this fact and link the overall material response with its micro-level. The development of various experimental techniques in the past decades made possible to access mechanical properties of various materials at submicron length scales. Nanoindentation plays an important role among them. This technique is based on the direct measurement of the load-displacement relationship. The depth of penetration starts from the level of nanometers. Although, nanoindentation was originally developed and used mainly for studying homogeneous materials like metals, coatings, films, glass, and crystal materials, the evolution of this method allows us to use it also for materials like concrete and other cementitious composites. The major studies can be found e.g. in [1], [2] and [5]. However, the interpretation of measured data is more complicated due to the large heterogeneity of cementitious composites. We will focus on cement paste (which is the base material of all cementitious composites) in the following.

* Ing. Ph.D., Department of Mechanics, Faculty of Civil Engineering, ČVUT v Praze, Thákurova 7, Praha 6, tel. (+420) 2435 4309, e-mail: jiri.nemecek@fsv.cvut.cz
** Prof. Ing. DrSc., Department of Mechanics, Faculty of Civil Engineering, ČVUT v Praze, Thákurova 7, Praha 6, tel. (+420) 2435 3869, e-mail: bittnar@fsv.cvut.cz

2 TESTING STRATEGIES

In contrast to usual indentation on metals, for example, cement paste is much more complex and also time-dependent material. From the microstructural point of view, cement paste is a highly heterogeneous material with several material phases. The most important are the hydrated phases (C-S-H gels that exist in two morphologies- high and low density [2], Portlandite, Ettringite and other minor phases), unhydrous phases (rest of clinker minerals) and porosity. Cementitious materials exhibit also significant creep that can affect evaluation of their elastic properties using standard procedures. This difficulty can be overcome by using long dwelling periods at the peak load. The material properties in this study are assessed for hydrated phases which occupy majority of the specimen volume. There are basically three testing strategies to assess micromechanical properties of individual phases in a heterogeneous material:

A. Producing of large number (grid) of indents that are larger than the characteristic phase dimension with subsequent statistical evaluation of overall material properties of all affected phases that were indented (phase compound).

B. Statistical indentation in which indents are produced over a large area but the dimension of a single indent is smaller than the characteristic dimension of individual phase. Subsequent deconvolution techniques can be employed for assessment of the individual phase properties [3], [4].

C. Pointed indentation to a specific material phase with indent's dimension smaller then the characteristic dimension of the tested phase. In this case, intrinsic properties of the phase (including intrinsic phase porosity) are obtained.

In this study, all three aforementioned approaches have been used and elastic properties evaluated by Oliver and Pharr method [4] compared. Since the hydrated phases exhibit not only elastoplastic but also viscous behaviour it was necessary to use long holding periods (around 60s) at the peak of the loading diagram. During this period so called "indentation creep" was measured (Fig. 3).

3 TEST SAMPLES

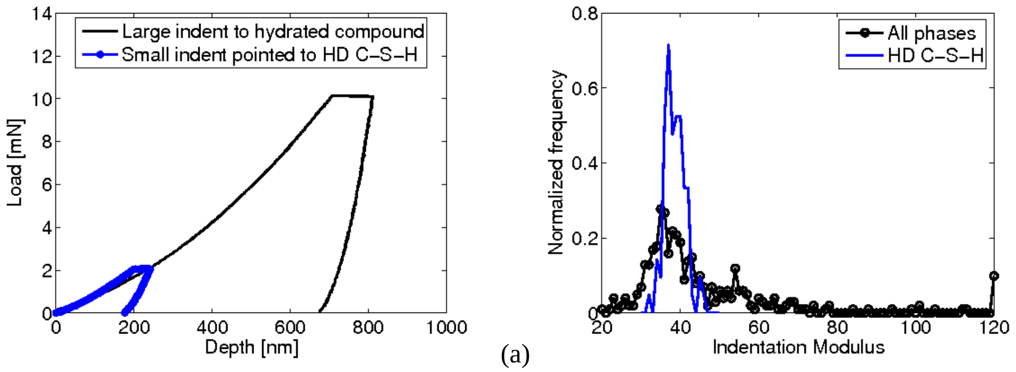
Alite (tricalcium silicate) paste samples were prepared. Water to cement ratio was 0.4. Samples were cured in water in 20 ^{o}C for 5 month. High degree of hydration can be supposed for such matured sample. Than the sample was dried and polished to achieve flat surface with the roughness 10-20 nm (RMS measured by AFM over 30×30 μm area).

4 RESULTS

For the first approach (A), a large grid of 100 indents was produced over the hydrated phases of cement paste. Indents lying in unhydrous phases were identified in ESEM and excluded from the study. The final depth of indents was around 700 nm (Fig.1a) which yielded in the surface dimension around 4 μm. Such indents' dimension affects usually more than one material phase and thus causes a physical homogenization (averaging) of properties. Overall modulus of elasticity for all the affected phases (mainly C-S-H gels and Portlandite) was measured to be 23.269 ± 3.093 GPa.

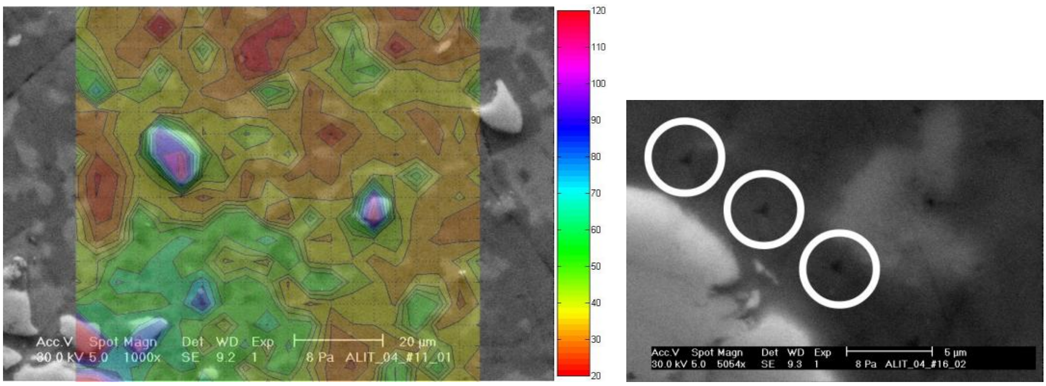
For the second approach (B), 400 small indents (around 200 nm in depth, Fig.1a) were produced with mutual distances 5 μm in between. The total area covered by indentation was 100x100 μm. The dimensions of indents was chosen to be below the characteristic phase dimension and therefore measurement provided information on (i) heterogeneity of the material properties and (ii) characteristic (intrinsic) material properties over the studied area. Results of indentation moduli are presented in the form of histogram in Fig. 1b. Several peaks defining mean values of indentation moduli of distinct phases can be found in this histogram. It is possible to apply deconvolution procedure to find Gaussian distributions of these phases [2], [3]. Comparison of the morphology taken in ESEM and the map of moduli is shown in Fig. 2a. Very good correlation of the data was achieved. Areas of hard clinkers and their surroundings created by high-density (HD) C-S-H can be easily recognized.

For the third approach (C), small indents similar to those used in (B) were pointed into one specific phase- HD C-S-H gel. This phase appears specifically around unhydrated clinker grains and it can be recognized in optics or in ESEM like a 5-10 μm rim (Fig. 2b). This pointed indentation resulted in much narrower histogram (Fig. 1b) of indentation moduli. Such a fact proves the existence of a homogeneous-like material phase within the tested length scale. The indentation modulus of this phase was 38.605 ± 2.569 GPa.



(a) (b)

Fig. 1 (a) Load-depth curve for large indent (P_{max}=10 mN) covering all hydrated phases of the cement paste and small indent (P_{max}=2 mN) with the size below the characteristic phase size. (b) Histogram of indentation moduli. (b1) Measurement over 100×100 μm area, (b2) pointed indentation to HD C-S-H.



(a) (b)

Fig. 2 (a) Map of the indentation modulus placed over the ESEM image of the same area of cement paste. (b) ESEM image of pointed indentation around clinker grain to HD C-S-H (indents are circled).

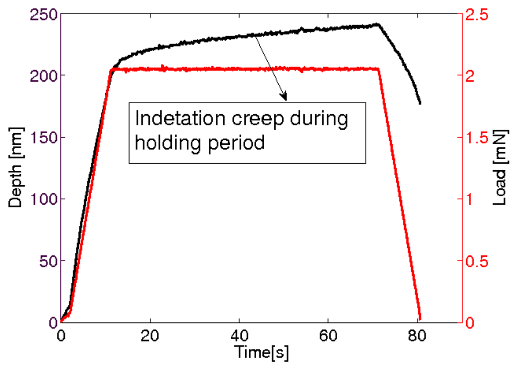


Fig. 3 Loading diagram (load vs. time) and indentation creep (depth vs. time) at holding period for HD C-S-H.

5 CONCLUSIONS

It was proved that nanoindentation can be used for assessment of intrinsic phases' properties of cement paste. The direct way of pointed indentation is possible only in some cases provided the phase can be easily distinguished in the microstructure. This was achieved for high-density C-S-H gel for which the elastic indentation modulus was assessed. If the direct measurement is not possible, statistical grid indentation can be used and individual phase properties can be deconvoluted from histogram plotted for all phases. Peaks in the histogram can be attributed to mean properties of individual material phases. For comparison, overall properties of the phase compound can be measured using grids with large indents. Short-time viscous properties in the form of indentation creep can be measured at the holding period of the loading diagram. During this stage, creep is manifested by all of the hydrated phases, mainly C-S-H gels.

ACKNOWLEDGEMENTS

Support of the Czech Grant Agency (No. 103/06/1856) and Ministry of Education of the Czech Republic (MSM 6840770003) are gratefully acknowledged.

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Reviewer: MSc. Jiří LUKŠ, Ph.D., VŠB - Technical University of Ostrava