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NANOINDENTATION OF CEMENT PASTES
NANOINDENTACE CEMENTOVÝCH PAST

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This paper reports about the new experimental technique for assessment of micromechanical properties of a material, nanoindentation. The technique itself and the method for evaluation of measurements is outlined briefly. Some unique experimental measurements conducted on Portland cement pastes using nanoindentation are reported.

Tento článek pojednává o nové experimentální technice pro stanovení mikromechanických vlastností materiálu, nanoindentaci. Stručně je vysvětlena tato technika a metoda pro vyhodnocení měření. Jsou ukázána některá unikátní měření s použitím nanoindentace uskutečněná na cementových pastách z Portlandského cementu.

Keywords *cement paste, concrete, nanoindentation, scanning electron microscopy.*

Klíčová slova *cementová pasta, nanoindentace, rastrovací elektronová mikroskopie.*

Introduction

The design of concrete structures must count on many physical phenomena. So far, the material properties of concrete have been studied on a macroscopic, i.e. structural basis without a fundamental knowledge of micromechanical material properties. However, nanoscience has been progressively growing in the recent decade. This growth was made possible with the aid of novel experimental techniques. Variety of such techniques for describing micro to nanostructure of the material have been developed such as infra-red spectroscopy, nuclear magnetic resonance, quantitative X-ray diffraction, environmental scanning electron microscopy (ESEM), atomic force microscopy, depth sensing indentation (DSI, nanoindentation) and others. Some pioneer work on assessment of microproperties of cement constituents using nanoindentation has been done (e.g. [1], [6]) but the basic knowledge of micromechanical properties in different conditions (such as high temperatures) is still lacking. The measurement of microproperties provides us fundamental information on the behavior of material phases. These microproperties can be considered as intrinsic material properties. Taking this basic knowledge of microproperties we are able to use upscaling techniques for assessment of macroscopic properties.

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This paper deals with cement pastes as an important constituent of concrete. Cement paste (hydrated Portland cement in our case) includes following main phases: hydrated silica clinkers, i.e. CSH (calcium silica hydrates), CH ($Ca(OH)_2$ called Portlandit), hydrated aluminate and ferrite phases, unhydrated clinker grains and pore system + water. The assessment of micromechanical properties of these constituents involves nanoindentation, ESEM analysis and evaluation of the results for selected structural phases.

Instrumentation

For all measurements we used Microtest nanoindenter made by Micro Materials, UK (see Fig.1). The indenter itself is a machine consisting of anti-vibration table, very stiff frame with a pendulum hanged on a frictionless pivot. The pendulum is equipped with a diamond tip on one side. A coil attracts the other side of the pendulum. The nanoindentation technique is based on the measurement of penetration of the diamond tip into the material. The diamond tip may have different shapes (pyramidal, spherical, flat...). For the present measurements we used so-called Berkowich indenter, which has a three-sided pyramidal shape with the side to edge inner angle $\approx 124^{o}$ and with a very sharp tip with the radius around 40 nm. The result of the measurement is a load versus depth of penetration diagram.

For microstructural analysis an environmental scanning electron microscope XL30 ESEM-TMP, Philips Ltd. was used. This microscope is able to work in high and low vacuum as well as in an environmental mode and it is suitable for testing of non-conductive samples like cement.

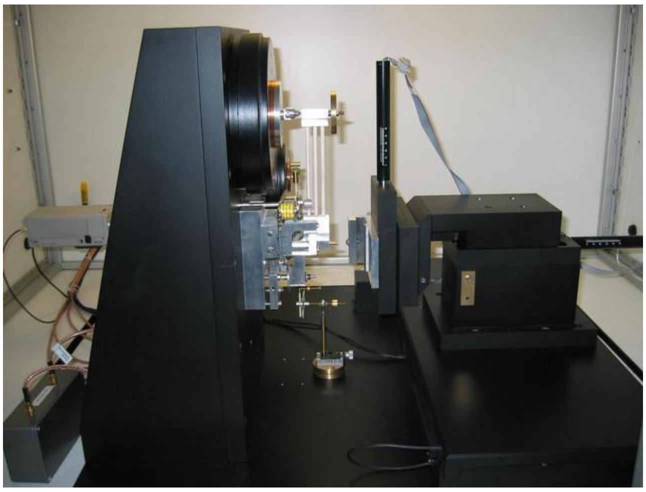

Fig. 1 Microtest nanoindenter (Micro Materials, UK).

Evaluation of measurements

The evaluation of micromechanical properties is based on the analysis of the load-depth diagram measured by the nanoindenter. The curve in the diagram has loading and unloading parts. Loading part of the curve contains elastoplastic response of the material. Elastic properties can be evaluated from an unloading part of the curve according to Oliver and Pharr [3]. The analysis is based on the analytical solution known for rotational bodies punched into the elastic isotropic half-space. Two elastic properties can be derived-elastic modulus E and hardness H. The effect of non-rigid indenter can be accounted for by defining a reduced modulus E_r:

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i}, \qquad (2)$$

where E and ν are tested material elastic modulus and Poisson's ratio, respectively. E_i and ν_i are indenter's parameters (for diamond: E_i=1141 GPa and ν_i=0.07). Since E and E_r values do not differ significantly in our case and moreover, ν for cement paste was not measured, only reduced moduli are used in the subsequent considerations.

Hardness is defined as follows:

$$H = \frac{P_{max}}{A}, \tag{3}$$

where P_{max} is the peak load and A is the projected area of contact at peak load.

Cement paste is microscopically very heterogeneous material. Thus, evaluation of results employs statistical evaluation of elastic properties for selected indents of the same structural phase. For this reason, using of electron microscope for evaluation of results is a necessary condition.

Measurements

Several measurements on Portland cement pastes (CEM-I 52,5 R) have been conducted. The major constituent of the hydrated cement paste is CSH gel and different amount of unhydrated clinkers according to hydration degree. These two structural phases have very distinct properties that can be documented in Tab. 1 where an example of statistical evaluation (based on ESEM analysis) for different constituents can be found. The difference between depth vs. load curve measured in CSH and in unhydrated clinker is depicted in Fig. 2.

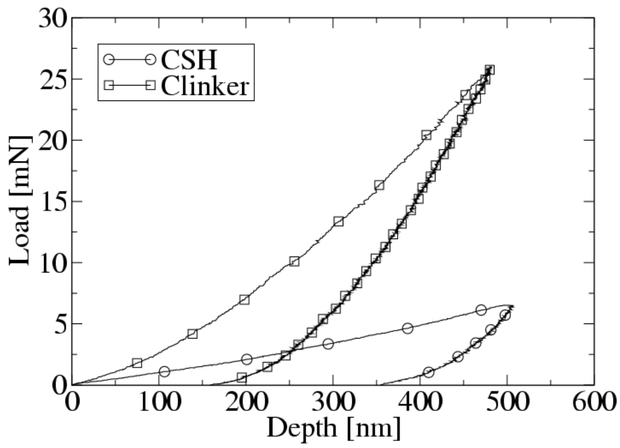

Fig. 2 Depth vs. load diagram for different cement paste constituents.

Tab. 1: Example of micromechanical properties of different constituents of Portland cement.

	CSH	unhydrated clinkers
Elastic modulus E [GPa]	33.644 ± 11.558	112.365 ± 21.258
Hardness H [GPa]	1.784 ± 0.815	8.397± 2.258

For experiments on a heterogeneous material like cement paste the measurement is usually arranged into a matrix to capture this heterogeneity. Such a matrix of indents in a cement paste can be seen in Fig. 3. An example of a single indent in cement paste is shown in Fig. 4. A typical pyramidal shape can be easily recognized at this ESEM image.

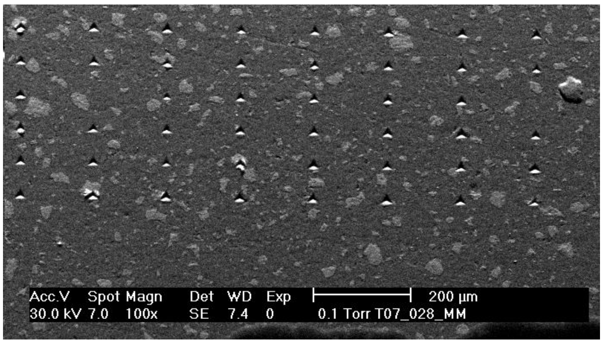

Fig. 3 Matrix of indents in a sample.

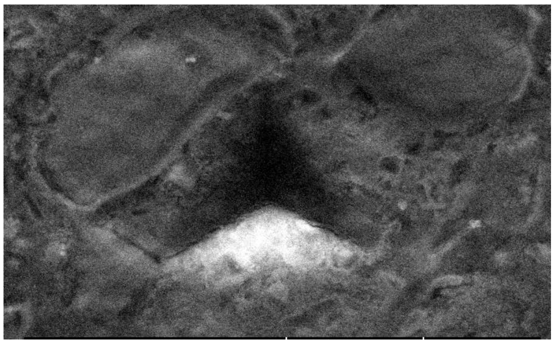

Fig. 4 Indent in CSH gel

Conclusion

The novel micromechanical experimental technique- nanoindentation- was described and its application to measurement of intrinsic micromechanical properties of cement pastes was shown. The technique can be utilized for variety of measurements that could not be conducted ever before since this technique enables us to access mechanical properties at the scale of individual material components.

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