Heat influence on micromechanical properties of cement pastes

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ABSTRACT: The paper deals with an experimental investigation of micromechanical properties by means of nanoindentation. The effect of the exposure to high temperatures is studied. Elastic properties of Portland cement paste samples are measured at room and at elevated temperatures up to 800 °C. Microproperties are evaluated mainly for CSH constituents of hydrated cement that occupy the majority of the volume.

Keywords: cement paste, concrete, nanoindentation, scanning electron microscopy, thermal load

1 INTRODUCTION

It is a well-known fact that concrete together with steel are one of the world's leading structural materials. The world's production of concrete and reinforced concrete structures is enormous in comparison with other materials. Nowadays, the production and the use of cementitious materials are well established and relatively cheap. This makes the material attractive for building industry although requirements put on the material are progressively growing due to the industrial and also environmental demands. The most important component used for concrete production is Portland cement that significantly influences resulting properties of the concrete mixture.

The design of concrete structures includes also the assessment of fire resistance. It is also a well-known fact that concrete undergoes significant changes when exposed to the high temperature loading. So far, the material properties of concrete subjected to high temperatures have been studied on a macroscopic, i.e. structural basis without a fundamental knowledge of micromechanical material properties. However, progress in the development of the material itself and in the better understanding of its behavior can be achieved only by extending the scale of investigation from macroscale to micro or ultimatively to nanoscale.

This will lead to both qualitative and also quantitative characterization of the properties at microlevel and will allow us to construct more accurate models based on this knowledge. The research on the micro/nanolevel was 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) and others.

The mechanical properties of concrete and its constituents (cement, aggregate, etc.) at the microlevel can be effectively studied by means of DSI, briefly nanoindentation. This technique is based on the measurement of the load-displacement relationship using a very sharp diamond tip pressed into the material. Nanoindentation was originally developed and used mainly for studying homogeneous materials like metals, coatings, films, glass, and crystals. However, the evolution of this method allows us to use it also for materials like concrete although the interpretation of measured data is more complicated due to the large heterogeneity of concrete and cement as well.

2 MOTIVATION

The behavior of concrete structure exposed to fire loading is of prior interest especially these days when terrorist attacks are encountered more frequently. A residual value of material properties after the fire is a necessary knowledge for designing repairs of a structure. An accurate modeling of concrete and its constituents can be hardly imagined without the knowledge of microstructural behavior. However, mechanical properties based on measurements at micro/nanoscale, i.e. crystalline level, are still lacking. This lead us to the research of micromechanical properties of cement pastes based on nanoindentation that is an effective and virtually the only one method for determination of the mechanical properties at this level.

3 DEGRADATION PROCESSES IN HEATED CEMENT PASTE

Concrete is a heterogeneous composite material. Its main macroscopic components are cement paste, aggregate, free water and pore system. When concrete is exposed to temperatures above 100 °C the free water evaporates and it tends to expand. It produces high pressures within the pore system and as a consequence of this multiple cracks develop. Further increase of temperature causes chemical decomposition of calcium hydrate and calcium carbonate.

This paper deals with cement pastes as the most important constituent of concrete. Similar situation as for the whole concrete can be found for cement paste. Cement paste is a hydrated Portland cement (in our case) which 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 again pore system + water. Rising the temperature of cement paste the free water evaporates at first around 105 °C and the decomposition of CSH gel (loss of water) takes place very soon around 130 °C. If the temperature is raised to about 480 °C decomposition of CH takes place according to formula:

$$Ca(OH)_2 \rightarrow CaO + H_2O \quad (1)$$

These chemical changes contribute to the degradation of the material. They are also related to the changes of mechanical properties of the affected constituents.

Particular differential thermal analysis (DTA) and thermogravimetry (TG) for our samples of cement paste were done. Results of the analysis are depicted in Figure 1. The upper curve (TG) shows large loss of water at the beginning around 100 °C then the loss of mass is progressive but smaller. Two main endothermic peaks in DTA curve show probably decomposition of CSH at 146 °C and decomposition of CH at 535 °C.

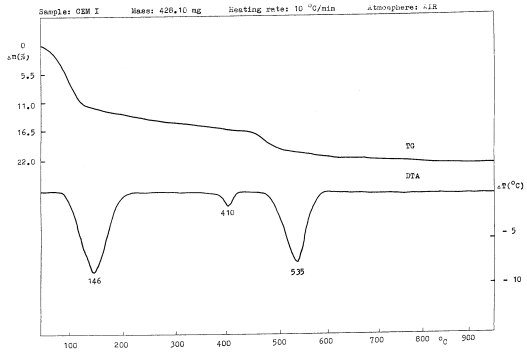

Figure 1. DTA and TG analysis of Portland cement paste CEM I-52.5. Three endothermic peaks at 146, 410 and 535 °C.

4 METHODS

All measurements were done on the cement paste samples with one selected composition. Specimens were cured in water and a flat smooth surface suitable for nanoindentation was prepared (see section 5). Then micromechanical properties were measured using nanoindentation. All specimens were tested twice. First, the nanoindentation at room temperature (28 °C) was performed. A series of 48 indents that were arranged into a matrix was made (see Figure 2). The approximate depth of an indent was 500 nm. The number of indents was necessary to capture heterogeneity of cement paste. Then the specimen was taken out of nanoindenter and ESEM analysis was performed to determine the location of individual indents.

After finishing of ESEM analysis the specimen was placed into the high temperature furnace and exposed to a given elevated temperature. Five temperatures were tested: 400, 500, 600, 700 and 800 °C. Then the sample was cooled down to room temperature. Finally, the sample was placed to nanoindenter and tested again in the same manner like before. Again ESEM analysis of indentation area was performed. Examples of ESEM analysis

are shown in Figure 3 and Figure 4 where an indent in CSH gel and in a large unhydrated clinker grain can be seen.

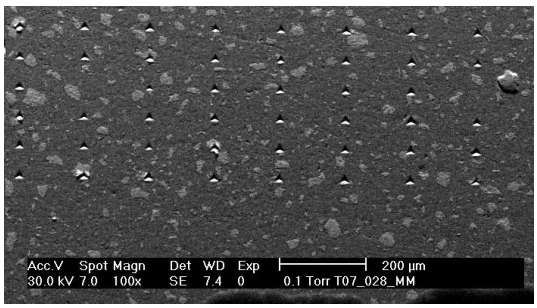

Figure 2. Matrix of indents in a sample at room temperature.

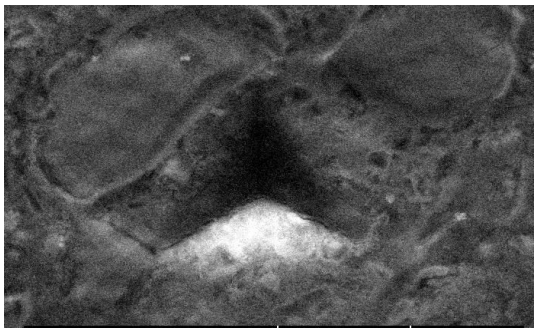

Figure 3. Indent in CSH gel (sample after heating to 800 °C).

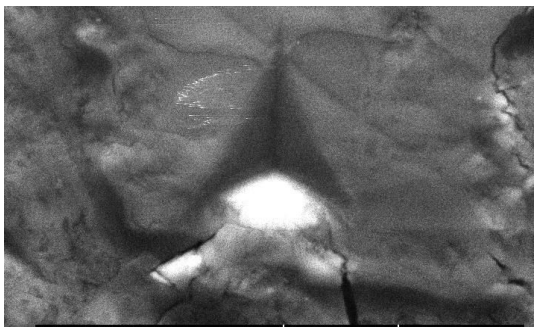

Figure 4. Indent in a large unhydrated clinker grain.

Micromechanical elastic properties of an individual indent were analyzed according to Olivier & Pharr (1992). Based on the ESEM analysis it was decided which location was indented and indents were divided into two major groups: indents in unhydrated clinkers and indents in CSH gel. It is also impossible to distinguish between hydration products only by morphological details seen in microscope. In the subsequent considerations, the term CSH gel is used in more general sense. As silica hydrates occupy majority of the volume (about 70%) this term is used for hydrated phases as a whole and it is also used for the product phases after the heat exposure (i.e. what it was CSH).

Statistical evaluation of microproperties was performed only for CSH data because the majority of indents were located in CSH gel. The comparison of microproperties for differently heated samples was done finally.

5 EXPERIMENTAL DETAILS

5.1 *Samples*

All samples were made of ordinary low-alkali sulfate resistant Portland cement CEM I-52.5 R (Hranice, CZ). Cement was mixed with water with the water/cement ratio w/c=0.4 by weight. The mixture was placed to small plastic cylindrical moulds with the volume 31 cm^3 and vibrated immediately after casting. After then, specimens were cured under the water for 42 days. After then they were stored in room conditions for approximately 14 days until they were tested. Before testing a 2 mm thick slice of a specimen was cut in the middle third of a cylinder.

5.2 *Preparation of samples*

The testing of micromechanical properties and behavior of materials like cement paste requires preparation of very flat and smooth surfaces. The surface roughness after the saw cutting and other defects caused by traditional methods of sample preparation is unacceptable for these purposes. Grains and dust remaining on the surface and high roughness may lead to serious misinterpretations for ESEM analysis and nanoindentation data analysis as well. The roughness of the surface must be measured in the scale of nanoindentation. It means we had to prepare the surface with maximum roughness of about tens to hundred nm because our indents were 500 nm deep. Otherwise, the indentation data could be contaminated and also ESEM analysis would became impossible.

Cement paste has low cohesion and using of routine grinding and polishing methods does not lead to acceptably flat and smooth surface. Suitable preparation techniques for the SEM-backscattered electron imaging and X-ray microanalysis were described in several papers, e.g. Detwiler et al. (2001), Kjellsen et al. (2003). We adopted some of these approaches. Our procedure was based on a combination of mechanical grinding and polishing on coarse to fine emery papers (320/600/1000/ 2000) and acrylate impregnation of the samples. At the end, specimens were grinded again on the finest

paper and washed in ultrasonic bath to remove all the dust. Also the acrylate was dissolved from the specimen. The resultant surface had the roughness about several tens of nm.

5.3 *Heat loading*

After the first indentation series at room temperature (28 °C) the specimen was placed into the high temperature furnace and exposed to a given elevated temperature. Five temperatures were tested: 400, 500, 600, 700 and 800 °C. The temperature rate for heating was 10°C/min and the final temperature was held for 1 hour. Then the sample was cooled down to room temperature. The time dependence of temperature elevation and drop is depicted in Figure 5. During the cooling period the sample was kept in the furnace until the room temperature was reached. The cooling tail is approximately exponential.

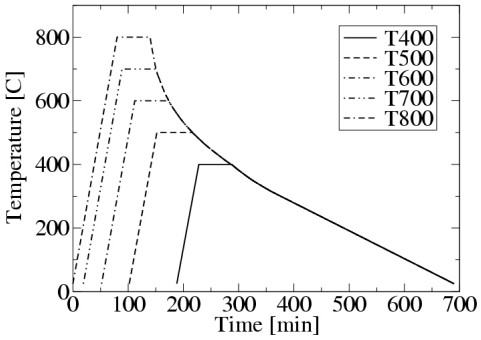

Figure 5. Time dependence of heat loading of samples.

5.4 *Instrumentation*

For all measurements, we used Microtest nanoindenter made by Micro Materials, UK (see Figure 6). 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 these 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 electron scanning 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.

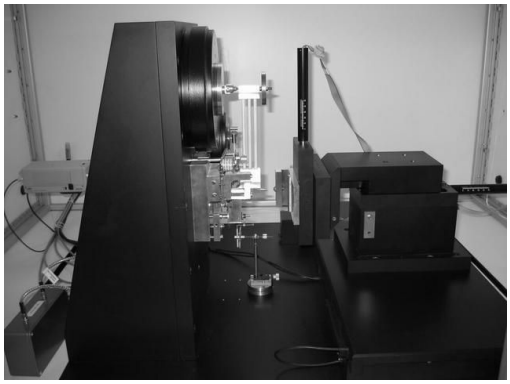

Figure 6. Microtest nanoindenter (Micro Materials ,UK).

6 RESULTS

6.1 *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 Olivier and Pharr (1992). 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:

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

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:

$$H = \frac{P_{\max}}{A}, \qquad (1)$$

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

Measured elastic properties serve for both quantitative and qualitative evaluation. It can be clearly compared how the material of specimens was deteriorated by elevated temperatures.

As it was mentioned above, statistical evaluation (mean values and standard deviations) of elastic properties was applied for selected indents of the same structural phase. This evaluation was used only for CSH gel because the majority of indents laid in CSH that occupied about 70% of the volume.

6.2 *Results of measurements*

Elastic properties were evaluated for each specimen twice as it was measured - at room temperature and after the exposure to elevated temperature. Always, some of indents laid in CSH and some in unhydrated clinkers. Results of the reduced elastic modulus for CSH are summarized in Table 1 and for hardness in Table 2 where the mean values and standard deviations can be found.

Table 1. Reduced elastic modulus measured at room temperature and after the exposure to higher temperature for CSH.

	At room temp. E_{28}	After temperature T exposure E_T	Ratio E_T/E_{28}
Specimen	GPa	GPa	-
T400	66.414 ± 9.867	59.095 ± 8.438	0.890
T500	58.703 ± 12.43	42.736 ± 15.174	0.728
T600	69.362 ± 10.076	46.830 ± 8.848	0.675
T700	65.667 ± 11.043	31.131 ± 9.076	0.474
T800	53.821 ± 6.867	23.946 ± 6.827	0.445

* Temperature T=400, 500, 600, 700 and 800 °C as indicated by the specimen notation.

Table 2. Hardness measured at room temperature and after the exposure to higher temperature for CSH.

	At room temp. H_{28}	After temperature T exposure H_T	Ratio H_T/H_{28}
Specimen	GPa	GPa	-
T400	2.717 ± 0.688	3.436 ± 1.052	1.265
T500	2.042 ± 0.625	2.125 ± 0.586	1.041
T600	2.411 ± 0.423	2.074 ± 0.617	0.860
T700	2.766 ± 0.693	1.578 ± 0.402	0.571
T800	2.566 ± 0.552	0.965 ± 0.268	0.376

* Temperature T=400, 500, 600, 700 and 800 °C as indicated by the specimen notation.

Due to the large heterogeneity of cement pastes even in one sample, it is impossible to obtain identical results from different samples measured at the same temperature, i.e. at the room temperature in our case. Therefore, relative changes in the given property are computed as a ratio between property at elevated temperature and room temperature for each sample. These relative changes can be found again in Tables 1 and 2. To see the trend in the property changes the values were plotted in Figure 7.

Properties of clinkers were not analyzed due to the small amount of data for them. However, from the qualitative point of view, it is clear that clinkers are much harder and have much higher elastic modulus then CSH gels. This is valid for room temperature as well as for elevated temperatures. The situation is illustrated in Figure 8 for selected representative curves of indents in clinker and in CSH gel. The diagram shows measured depth vs. force curves plotted for room and for elevated temperatures.

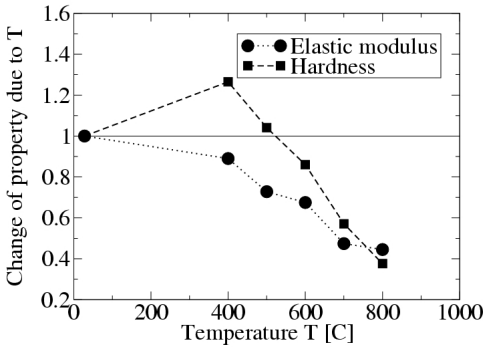

Figure 7. Diagram of relative change of reduced elastic moduli (E_T/E_{28}) and hardness (H_T/H_{28}) due to temperature loading at given temperature T.

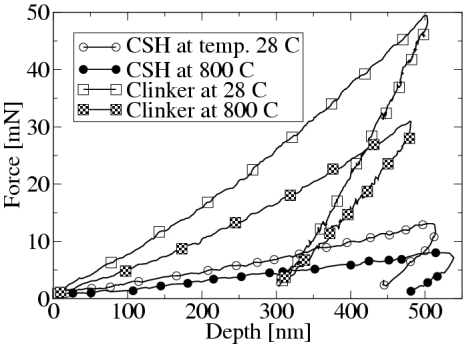

Figure 8. Depth vs. load diagrams for CSH and for clinker before and after temperature loading.

It must be also mentioned that sample surface (originally flat and smooth) was deteriorated and full of microcracks after the heating. This is shown in Figure 9 where the sample after heating to 800 ^{o}C with the matrix of indents can be seen. If an indent laid in such a microcrack caused by high temperature, it was excluded from further evaluation.

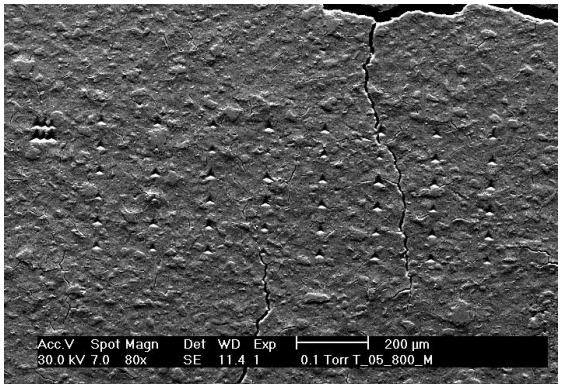

Figure 9. Deterioration of originally flat relief and microcracks visible in ESEM after 800 ^{o}C exposure.

6.3 *Discussion on results*

As it was expected, the temperature loading has a significant influence on micromechanical properties of cement pastes. Due to heat loading and chemical changes in the material described above the material is deteriorated. The loss of free water above 100 ^{o}C, the loss of water from CSH gels (146 ^{o}C according to DTA) and finally decomposition of CH at 535 ^{o}C cause mass and volume changes. Moreover, thermal dilatation that may cause further damage is present in the material. The degradation of elastic properties can be clearly seen in the whole temperature range. For example, elastic modulus drops down to 45% (see Figure 7) when the sample is exposed to 800 ^{o}C. The decreasing trend of this property is the same for the whole temperature range between 400 and 800 ^{o}C. The situation is different for hardness. It increases to 400 ^{o}C and then decreases towards 800 ^{o}C. The loss of water and strengthening of the microstructure due to temperatures before 500 ^{o}C cause the hardening in the beginning probably. But after 500 ^{o}C, rising of temperature disintegrates the material. This leads to significantly lower hardness towards 800 ^{o}C (38% of the original value, see Figure 7).

7 CONCLUSIONS

Micromechanical properties of selected Portland cement paste (CEM-I 52.5 R) were investigated by means of nanoindentation and environmental scanning electron microscopy. The properties were studied at room temperatures and after the exposure to high temperatures form 400 ^{o}C up to 800 ^{o}C. It was found that mechanical properties change gradually with rising temperature and accompanying chemical changes in the material. Generally, the properties are degrading as the high temperature deteriorates the material. At 800 ^{o}C, elastic modulus decreases to 45% of the original value. The hardness of cement paste increases slightly for temperatures before 500 ^{o}C and then drops down to 38% at 800 ^{o}C.

ACKNOWLEDGMENTS

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