Micromechanical properties of cement pastes at elevated temperatures

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Summary

This paper reports about an experimental investigation of micromechanical properties of cement pastes. The effect of exposure of cement pastes to high temperatures is studied. Elastic properties of Portland cement paste samples were measured at room and at elevated temperatures up to 800 ^{o}C. The assessment of microproperties is based on nanoindentation results and evaluated mainly for CSH constituents of hydrated cement that occupied the majority of the volume.

Introduction

The design of concrete structures must count on many physical phenomena. It includes also the assessment of fire resistance, for example. Concrete and its components undergo multiple chemical and structural changes when exposed to high temperatures. 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, 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 microproperties of cement constituents using nanoindentation has been done e.g. [2], [7] but the basic knowledge of micromechanical properties at elevated temperatures is still lacking.

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. Rising the temperature of cement paste the free water evaporates at first around 100-105 ^{o}C and the decomposition of CSH gel (loss of water) takes place very soon

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around 130 °C. If the temperature is raised to about 480 °C decomposition of CH takes place according to formula:

$$Ca(OH)_2 \rightarrow CaO + H_2O \tag{1}$$

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

Methods

An ordinary Portland cement samples were chosen for this study. Micromechanical properties were measured by means of 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 1). 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 selected: 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. Finally, the sample was placed to nanoindenter and tested again in the same manner like before. Again ESEM analysis of indentation area was performed. An example of ESEM analysis is shown in Figure 2 where an indent in CSH gel can be seen.

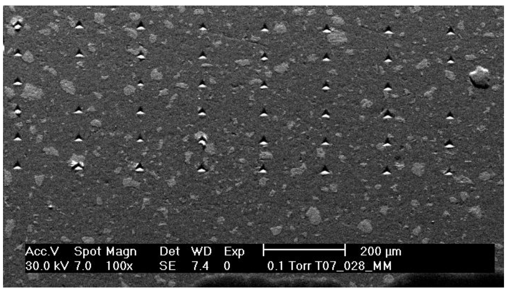

Figure 1. Matrix of indents in a sample at room temperature.

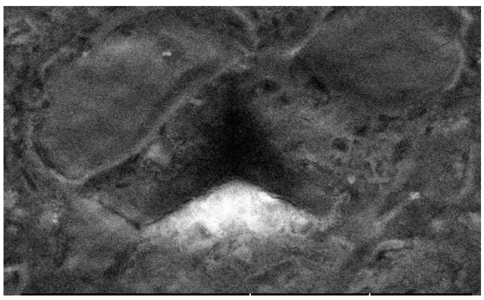

Figure 2. Indent in CSH gel (sample after heating to 800 °C).

Micromechanical elastic properties of an individual indent were analyzed according to Oliver & Pharr [4]. 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.

All samples were made of Portland cement CEM I-52.5 R with the water/cement ratio w/c=0.4 by weight. Specimens were 42 days cured in water before testing. Special attention was paid to the surface preparation of specimens, which plays a key role for ESEM analysis and for interpretation of nanoindentation data. For all measurements, we used Microtest nanoindenter made by Micro Materials, UK equipped with three-sided pyramidal Berkowitch indenter. For microstructural analysis an environmental electron scanning microscope XL30 ESEM-TMP, Philips Ltd. was used.

Results

To assess the decomposition temperatures, the differential thermal analysis (DTA) and thermogravimetry (TG) for our samples of cement paste were done. Results of the analysis are depicted in Figure 3. The upper curve (TG) shows large loss of water at the beginning around 100 ^{o}C then the loss of mass is progressive but smaller. Two main endothermic peaks in DTA curve show probably decomposition of CSH at 146 ^{o}C and decomposition of CH at 535 ^{o}C. The minor peak at 410 ^{o}C can be attributed to some impurity decomposition.

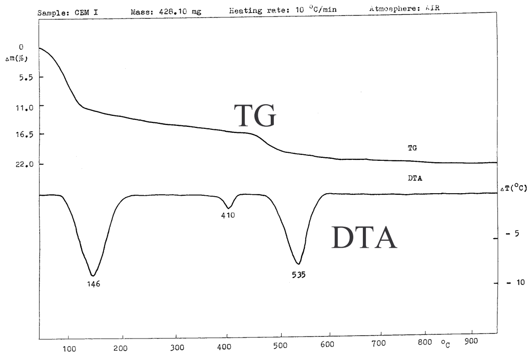

Figure 3. DTA and TG analysis of Portland cement paste CEM I-52.5. Three endothermic peaks at 146, 410 and 535 ^{o}C.

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 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. Elastic modulus measured at room temperature and after the exposure to higher temperature for CSH. All values are in GPa and T*x* refers to specimen exposed to *x* ^{o}C.

Specimen	At room temp. E_{28}	After temp. T exposure E_T	Ratio E_T/E_{28}
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 ± 8.84	0.675
T700	65.667 ± 11.043	31.131 ± 9.076	0.474
T800	53.821 ± 6.867	23.946 ± 6.827	0.445

Table 2. Hardness measured at room temperature and after the exposure to higher temperature for CSH. All values are in GPa and T*x* refers to specimen exposed to *x* ^{o}C.

Specimen	At room temp. H_{28}	After temp. T exposure H_T	Ratio H_T/H_{28}
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

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 4.

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 5 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.

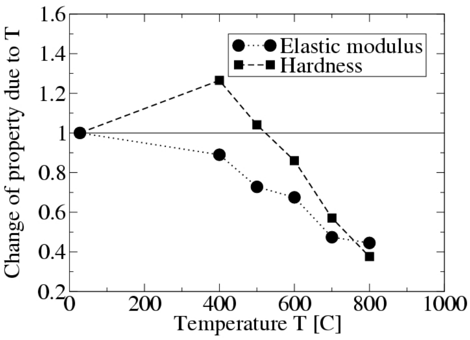

Figure 4. Diagram of relative change of elastic moduli (E_T /E_{28}) and hardness (H_T /H_{28}) due to temperature loading at given temperature T.

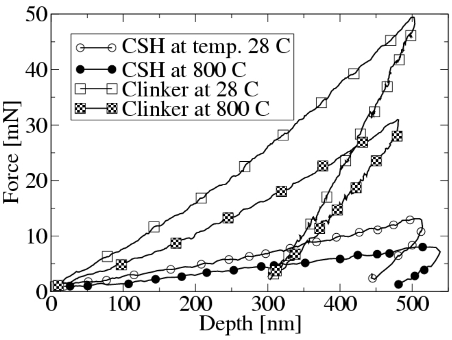

Figure 5. Depth vs. load diagrams for CSH and for clinker before and after temperature loading.

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 and chemically combined water causes 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 4) 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 4).

Conclusions

Micromechanical properties of 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.

Acknowledgements

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