Cement and Concrete Composites 73 (2016) 164–173

Contents lists available at ScienceDirect

Cement and Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Tensile strength of hydrated cement paste phases assessed by micro-bending tests and nanoindentation

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ARTICLE INFO

Article history:
Received 14 October 2015
Received in revised form
1 July 2016
Accepted 15 July 2016
Available online 18 July 2016

Keywords:
Cement
Hydration products
Micro-beam
Tensile strength
Fracture energy
Nanoindentation
Focused ion beam

ABSTRACT

The paper is focused on the experimental investigation of cement paste's tensile strength and related mechanical properties at the micrometer level. Small scale specimens with micrometer dimensions in the form of cantilever beams having a triangular cross section and ≈20 μm in length are fabricated by means of a focused ion beam and tested in bending with the aid of a nanoindenter. Elastic properties are evaluated from both bending and nanoindentation tests for all the phases with very close agreement. The phase separation is performed with SEM-based image analysis and the deconvolution of grid nanoindentation results. The load-deflection curves of bent beams are monitored up to the failure for distinct microlevel phases, namely for inner and outer products and Portlandite. The tensile strength of the phases is directly derived from the load-deflection curves in the range of 264 MPa (for the outer product) to 700 MPa (for the inner product and Portlandite). Moreover, the load-deflection curves are used for the supremum estimates of fracture energies for individual hydrated cement phases. Low values of the energies in the range of 4.4 – 20 J/m^2 were found. The values obtained experimentally in this paper correspond well with those published in recent multiscale or molecular dynamics models.

1. Introduction

Concrete is the most widespread civil engineering material in the world. The main binding component of this composite material is Portland clinker, which can be blended with slag, fly-ash, calcium carbonate, microsilica and other supplementary materials that serve as fillers and/or pozzolanic reactants [1]. Other components include water, aggregates and a variety of possible admixtures such as fibers. Concrete is also a composite with a hierarchical microstructure that comes both from the mixture of different components and from hydration reactions that evolve in time. Its mechanical properties are largely affected by various factors at all composite levels. The most important ones include the initial binder type, inclusions type and content, the air void content and the extent of interfacial zones between individual phases. To reduce the complexity of the material microstructure, concrete is usually treated with multi-scale models that must span over a range of levels starting from nanometers to meters [2–4].

At the microlevel, the main binding component, i.e. the hydrated cementitious matrix, is composed of a few main constituents: hydration products (known from cement chemistry as Calcium-Silica-Hydrates, labeled hereafter as C-S-H gels; other hydrates, e.g. ettringite-AFt, monosulfate-AFm, Calcium-Aluminate-Hydrates (C-A-H); Portlandite $Ca(OH)_2$ (labeled as CH); porosity; anhydrous clinker minerals and some other minor (mechanically insignificant) phases [1,5,6].

Concrete is used due to its many advantages that include practicality (e.g. easy shaping, local availability of source materials), economical issues (i.e. its relative low-cost compared to other materials like metals), very good mechanical properties (e.g. high stiffness, high compressive strength) and durability.

One of the weak points of concrete is its relatively low tensile strength (typically a few MPa). However, the theoretical strength of quasibrittle materials increases as the sample size or scale decreases. This is valid for finer scales (nano- and micrometer), where

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http://dx.doi.org/10.1016/j.cemconcomp.2016.07.010
0958-9465/

previous modeling showed the tensile uniaxial strength of low- and high-density C-S-H phases to be $C-S-H_{LD}$ = 66 MPa and $C-S-H_{HD}$ = 107 MPa and for the C-S-H globule to be as high as 320 MPa [7,8]. Since such tensile strengths have never been measured experimentally on finer scales, the purpose of this work is to directly measure them on individual components of hydrated cement paste. This is achieved by fabricating small cantilevers by the Focused Ion Beam technology, FIB, and performing direct bending tests with the aid of a nanoindenter. This pioneering work offers new insights into the material strength origin and gives valuable quantitative information for numerical models that need to be calibrated on finer scales.

By now, the mechanical quantification of microlevel components has been provided almost exclusively by nanoindentation [9]. This technique allows penetrating specimen's surface by a sharp indenter leading to the evaluation of mechanical information from shallow depths, typically below 1 μm on cement components. Nanoindentation has been successfully used to assess the elastic stiffness of individual phases at the submicron level of cement paste. The elastic moduli of anhydrous clinker minerals were measured, for example, by Velez et al. [10] and Němeček [11]. The elastic moduli of C-S-H phases in two characteristic densities [12], low- and high-density C-S-H gels, were firstly reported by Constantinides and Ulm [13] and confirmed by other researchers on various cementitious systems, e.g. Refs. [11,14,15]. The elastic stiffness of individual cement components was studied in conjunction with calcium leaching providing the evidence of two characteristic C-S-H densities [13]. Nanoindentation was employed to extract, for example, the phase elastic properties of various heterogeneous systems [16], high performance concretes [4] and interfacial transition zones [17]. The grid indentation technique is usually used to deal with the statistical heterogeneity of the cementitious matrix [16,18–20]. The papers so far have mentioned the use of mechanical polishing to prepare the surface of samples for indentation and the spatial resolution of measured mechanical properties is kept within a few hundred nanometers. Local mechanical characterization is also provided with a higher resolution by peak-force tapping AFM on a FIB-prepared specimen surface [21].

Nanoindentation can also be used as a versatile tool to load small scale specimens that are fabricated by either mechanical means or by FIB on micron or submicron levels. Typically, the micro-pillar or micro-beam geometry is prepared by FIB and the nanoindenter serves as a compression tool. This technique is used in material science (applied mostly to metals, various thin films and electronics components) to study the basic deformation mechanisms and behavior of small material volumes and to derive elastic, plastic and fracture material properties [22,23]. An application of a precision saw cutting for fabrication of micro-pillars in cement paste, subsequent nanoindentation and modeling of the failure mechanism can be found in Ref. [24]. The paper describes breaking of pillars without assessment of strength or breaking load. So far, however, the compression of micro-pillars or micro-bending tests have rarely been used in cementitious materials due to technical and instrumental demands. The first attempt to use FIB milling on cement paste and to quantify its strength from micro-machined beams was published by Chen et al. [25]. The authors presented an early data received from a single FIB-milled cantilever in cement paste loaded with AFM. They found the flexural strength of cement paste to be as low as 2.67 MPa which seems to be in contradiction to scaling of strength to micrometers in quasi-brittle materials [26].

In this work, the micro-bending tests of FIB prepared samples were adopted and individual cement paste phases quantified for the first time with the nanoindenter. A much larger extent of the measurements and information on phases' elasticity, tensile strength and fracture properties is presented in this paper.

2. Materials and methods

2.1. Cement paste

Hydrated cement paste samples were prepared from Portland cement CEM-I 42,5R (taken from the Heidelberg cement plant in Mokrá, Czech Republic). The chemical composition of the cement is shown in Table 1. The fineness of the cement, characterized by the Blaine specific surface, was 306 m^2 kg^{-1}. The cement was mixed with water to yield a water/cement ratio of 0.4, stirred and vibrated to release entrapped air. The mixture was poured into small cylindrical plastic moulds (height = 60 mm, diameter = 30 mm). The next day after casting, the samples were demoulded, placed into tanks with water and stored. The storage time was 7 years at an average laboratory temperature of 22° C. After such a long time, a very high degree of hydration can be anticipated meaning the paste contains a minimum amount of anhydrous components.

Before testing, the samples were cut into 5 mm thick slices by a precision diamond saw, dried in ambient conditions (with the relative humidity below 40%) and mechanically polished with a series of SiC papers down to the grit size #4000 in the Struers® metalographic polishing system. Then, the samples were observed with the Scanning Electron Microscope (SEM) for the volumetric quantification of individual material phases and micromachined with FIB. The samples were stored in an inert environment (Argon gas) to suppress carbonation between the tests.

2.2. Preparation of micro-beams by FIB

FIB was chosen to fabricate cantilever micro-beam specimens from cement paste samples. This technique allows precise shaping of the material at the microscale with physical limitations caused by the inaccessibility of some surfaces to the ion beam and possible redeposition of the sputtered material in a confined space. For these reasons, rectangular cross sections of the beams are not technically feasible and a triangular cross-section was chosen as the best geometry for micro-machining via FIB. The characteristic cross sectional depth of the beams was chosen to be around 3 – 4 μm while the cantilever length was around 20 μm. Such dimensions allow precise fabrication without defects or FIB artifacts and are still small enough to be produced within a single material phase. The ratio of length to transverse dimensions is approximately 5 in order to minimize the shear effect and to be able to deform the cantilever mostly in pure bending. The scheme of the beam geometry and loading direction is depicted in Fig. 1.

All micro-beams were prepared by the FEI Quanta 3D FEG dual beam instrument combining SEM and FIB. The FIB is a well-established technique that uses a finely focused beam of gallium ions for precise micromachining of various materials [27]. FIB milling procedure was optimized to suppress the redeposition of sputtered material on the micro-beam surface [28]. The final milling step was done at an accelerating voltage of 30 kV and a current of 1 nA. After FIB milling, the micro-beams were observed by SEM to verify their dimensions. Simulations carried out by SRIM 2013 [29] revealed that Ga^+ ions accelerated to 30 kV penetrate into the cement paste ≈36 nm deep on average. This introduces an affected layer ≈1% of a micro-beam depth. Therefore, the influence

Table 1
Chemical composition of the used cement (XRD data supplied by the manufacturer).

Component	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	TiO_2
wt %	63.77	20.51	4.74	3.3	1.05	0
Component	K_2O	Na_2O	SO_3	MnO	free Ca	
wt %	0.95	0.15	3.07	0.09	0	