Construction and Building Materials 105 (2016) 496–502

Contents lists available at ScienceDirect

Construction and Building Materials

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

Micromechanical investigation of magnesium oxychloride cement paste

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HIGHLIGHTS

- Micro-mechanical properties of the reaction product, phase 5, were determined.
- Elastic modulus at micro- and macro-scales were correlated by multiscale model.
- Acicular shape of the phase 5 reaction product was considered in multiscale model.

ARTICLE INFO

Article history:
Received 27 September 2015
Received in revised form 9 December 2015
Accepted 22 December 2015

Keywords:
Magnesium oxychloride (MOC) cement
Micromechanical properties
Microstructure
Multiscale modeling

ABSTRACT

In this study, nanoindentation coupled with scanning electron microscopy technique for the microstructural and micromechanical characterizations were applied on the magnesium oxychloride (MOC) cement paste. For the first time, micromechanical properties of the reaction product, phase 5 ($5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$) in MOC cement system were investigated. It was determined that the average indentation modulus and hardness of phase 5 were 32.5 ± 4.2 GPa and 1.03 ± 0.19 GPa, respectively. Moreover, the elastic modulus of the MOC cement paste at micro- and macro-scales were further correlated, which built a framework for predicting its macroscopic elastic modulus.

1. Introduction

Magnesium oxychloride (MOC) cement, also known as Sorel cement, was invented shortly after Portland cement in 1867 [1]. As documented in the previous literatures [1–6], this air-dried chemically bonded cement has many superior properties to ordinary Portland cement, such as fast setting, high mechanical strength, good resistance to abrasion and fire, low thermal conductivity and excellent bonding ability to a wide range of fillers. By virtue of these obvious performance advantages, MOC cement has been conventionally used for making industrial floors [1–3], grinding wheels [1], and a variety of panels with different specific functions, such as decoration, fire protection, sound and thermal insulations [1–6]. More recently, new applications of MOC cement have been further explored. It can be used as bio-material [7] and solidification/stabilization agent for sewage sludge [8].

Magnesia (MgO), magnesium chloride ($MgCl_2$) and water (H_2O) are the three essential starting raw materials for fabricating MOC cement-based composites. With a through-solution reaction in this ternary system of $MgO–MgCl_2–H_2O$, four primary composition phases could be generated. They are the phase 2 ($2Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O$), phase 3 ($3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$), phase 5 ($5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$) and phase 9 ($9Mg(OH)_2 \cdot MgCl_2 \cdot 5H_2O$) [1]. Temperature plays a key role on governing the formations and stabilities of these four phases [1,2,9,10]. Phases 3 and 5 could be well formed and stably exist when the curing temperature is below 100 °C; nevertheless, phases 2 and 9 are only stable when curing temperatures are beyond 100 °C [1]. Moreover, molar ratio between MgO and $MgCl_2$ ($MgO/MgCl_2$), and that between H_2O and $MgCl_2$ ($H_2O/MgCl_2$) are the other two important factors affecting the formations of reaction products [1]. Among the above-presented four types of reaction products, phase 5 has been widely reported and considered as the most preferable one, as it can provide the best mechanical properties [1,2]. Till now, the microstructural information of phase 5, regarding its morphologies, crystal habits, grain sizes and elemental compositions, has been reported [1–10]. However, other equally important microstructural mechanical information of phase 5, like its local elastic properties and hardness, has been far less reported. This is of great research significance, as it can set a basis for much better and deeper understanding and improving the macroscopic behaviors of MOC cement-based composites.

Nanoindentation is an effective and powerful tool for determining the local elastic properties and hardness of material at micro- and nano- scales. During the last decade, nanoindentation has been

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http://dx.doi.org/10.1016/j.conbuildmat.2015.12.182
0950-0618/

popularly used for studying the microstructural mechanical properties of a variety of cementitious materials, such as synthesized calcium-silicate-hydrate, pure Portland cement pastes, mineral admixture blended cement pastes, alkali-activated cementitious materials, aggregate and fiber reinforced cement-based composites [11,12]. Consequently, a lot of valuable microstructural mechanical information regarding the local indentation modulus, hardness and creep compliance of these cementitious materials has already been well documented [11]. Considering the prominent benefits of nanoindentation that can provide a deep insight into the microstructural mechanical information of cementitious materials, it was employed in this study for investigating the still unveiled microstructural mechanical information of the reaction product in the MOC cement system. In this study, micromechanical and microstructural properties were determined by using the nanoindentation, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and mercury intrusion porosimetry (MIP). The elastic moduli of the MOC cement paste at micro- and macro-scales were correlated through application of the micromechanical approach with the consideration of acicular shape of the reaction product.

2. Experimental

2.1. Materials and mix proportion

The starting raw materials for preparing the MOC cement paste included light-burnt magnesia powder, magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), and tap water. The light-burnt magnesia powder was supplied by Jinan Magnesia-Carbon Brick Plant Co. Ltd., Shandong, China. Chemical compositions of the solid raw materials are provided in Table 1. The magnesium chloride hexahydrate was dissolved in water before use. The used $MgO/MgCl_2$ and $H_2O/MgCl_2$ molar ratios were 11 and 15, respectively.

2.2. Testing methods

2.2.1. Micro-characterizations

The crystalline phases of the MOC cement paste at 28 days were determined by XRD (PAnalytical X'pert Pro) method. The powder sample was prepared by crushing, grinding the MOC cement paste, and passing it through a sieve with a screen aperture of 75 μm. Furthermore, micro-morphology of the reaction product in the MOC cement paste at 28 days was characterized by SEM instrument (JSM 6390) equipped with EDX detector. The sample was sputter with gold coating before the SEM characterizations. The pore microstructure of the MOC cement paste at 28 days was determined by MIP method.

2.2.2. Micromechanical properties

In this study, nanoindentation test was employed for determining the micromechanical properties of the MOC cement paste at 28 days. According to the above-presented mix proportion, the MOC cement paste was prepared and cast in a plastic cubic mould with the dimensions of $40 \times 40 \times 40$ mm^3. It was cured in air at ambient temperature 24 °C and relative humidity 50% for 28 days, then cut into much smaller dimensions of $10 \times 10 \times 10$ mm^3. Surface of the obtained small cubic sample was carefully polished before the conduction of nanoindentation test. The sample polishing procedure could be generally divided into the following three steps. Firstly, the sample surface was polished using silicon carbide abrasive papers (400, 800 and 1200 grit) in order. As MOC cement-based materials are very sensitive to water, oil-based suspension instead of water was used during this polishing step. Afterwards, the sample surface was further polished using oil-based diamond suspensions (3, 1, and 0.25 μm), which was for obtaining a more smooth surface. Finally, this well-polished sample was placed in acetone and cleaned in an ultrasonic bath for 2 min to remove possible debris and suspension residues on the surface. The residual unreacted $MgCl_2$ in the MOC cement paste could be regarded as very small, as it was unable to be detected by XRD test. The detailed XRD result of this 28-day air curing MOC cement paste will be given in the latter part of this work. Therefore, this short 2 min acetone cleaning procedure could be considered having little impact on changing the microstructure of this MOC cement paste. Fig. 1 shows the SEM image of the polished MOC cement paste, where the residual indentation impressions can be clearly seen.

A Triboindenter equipped with a Berkovich diamond tip was used to characterize the microstructural mechanical properties of the MOC cement paste. Before the nanoindentation tests, the Triboindenter was calibrated on a standard sample (fused quartz). Fig. 2 demonstrates the loading mode employed in this study and the corresponding typical load–depth curve. As shown in Fig. 2(a), the loading mode included two loading processes. The first loading process with the maximum load of 2 mN was used for determining the micromechanical parameters, including indentation modulus (M) and hardness (H). Meanwhile, the second loading process with the maximum load of 10 mN aimed for better observing the indentation impressions under SEM. In order to eliminate potential mechanical interaction effect between the indents, a large spacing of 20 μm was used in both the lateral and vertical directions. Based on the determined load–depth curve that is typically presented in Fig. 2(b), the above-mentioned indentation modulus (M) and hardness (H) can be calculated as follows

$$M = \frac{1}{2}\left(\frac{dp}{dh}\sqrt{\frac{\pi}{A}}\right)\bigg|_{h=h_{\max}} \tag{1}$$

$$H = \left(\frac{p}{A}\right)\bigg|_{h=h_{\max}} \tag{2}$$

where p and h are the indentation load and the indentation depth, respectively; $h_{\max}$ is the maximum indentation depth; and A is the projected contact area that can be extrapolated from indentation depth h through Oliver and Pharr's method [13]. It is known that indentation modulus (M) can be correlated to the material elastic modulus (E) and Poisson's ratio (ν) through the following equation [14]

$$\frac{1}{M} = \frac{1-\nu^2}{E} + \frac{1-\nu_{tip}^2}{E_{tip}} \tag{3}$$

where E_{tip} is elastic modulus of the indenter tip; and ν_{tip} is Possion's ratio of the indenter tip. The E_{tip} and ν_{tip} of diamond tip are 1141 GPa and 0.07, respectively. Obviously, the diamond tip is far more rigid than the investigated MOC cement paste; hence, the above-presented Eq. (3) can be reasonably simplified as follows

$$M = \frac{E}{1-\nu^2} \tag{4}$$

The hardness (H) is related to yield strength of the local material; and, the hardness-to-yield strength ratio depends on material types. All the nanoindentation tests were conducted under ambient condition (typically 23 °C, 50% relative humidity). On the sample, a total of 800 nanoindentation tests were performed over two randomly selected surface areas. After the nanoindentation tests, the sample was sputtered with gold coating and further characterized by SEM instrument (JSM 6390) equipped with EDX detector.

3. Results and discussion

3.1. Compositions and microstructure of the MOC cement paste

Fig. 3 presents the XRD pattern of the MOC cement paste at 28 days. In Fig. 3, magnesia and phase 5 with strong characteristic peaks can be obviously seen. It clearly informs that in this investigated MOC cement system, phase 5 rather than other crystals, like phase 3 or brucite, could be considered as the only principal reaction product. Stoichiometrically, the formation of phase 5 only requires the $MgO/MgCl_2$ molar ratio equal to 5; while, higher molar ratios have been commonly employed in practice [1–9]. This could be the attributed reason for the seldom observed magnesium chloride in most mature hardened MOC cement systems with curing periods of 28 days or even more [1–9]. The XRD pattern shown in Fig. 3 well agrees with those previous findings [1–9], where no magnesium chloride crystal phase can be found. Therefore, this investigated MOC cement paste at 28 days could be generally considered having two solid phases, which are the residual unreacted

Table 1
Chemical compositions of the solid raw materials [6].

Material	MgO	SiO_2	CaO	Fe_2O_3	MnO	SO_3	$MgCl_2$	$CaCl_2$	KCl	NaCl	H_2O
Magnesia	93.63	2.98	2.33	0.55	0.14	0.37	–	–	–	–	–
$MgCl_2 \cdot 6H_2O$	–	–	–	–	–	–	45.8	1.3	0.3	0.6	52