Micron 107 (2018) 43–54

Contents lists available at ScienceDirect

Micron

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

Specimen preparation for nano-scale investigation of cementitious repair material

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ARTICLE INFO

Keywords:
Specimen preparation
Focused ion beam
Cementitious materials
Scanning Transmission Electron Holography Microscopy (STEHM)
Electron diffraction pattern

ABSTRACT

Cementitious Repair Materials (CRMs) in the construction industry have been used for many decades now and has become a very important part of activities in cement world. The performance of some of these CRMs when applied to retrofitting concrete structural elements is also well documented. However, the characterization of some of the CRMs at the micro- and nano level is not fully documented. The first step to studying materials at the microscopic level is to be able to fabricate proper specimens for microscopy. In this study, a special and newly developed class of CRM was selected and fabricated by Focused Ion Beam (FIB) using well-known "Lift-out" technique. The prepared specimen was later examined using various analytical techniques such as energy dispersive x-ray analysis using one of the highest and most stable Scanning Transmission Electron Holography Microscopy (STEHM) around the world. This process enabled understanding of the composition, morphology, and spatial distribution of various phases of the CRM. It was observed that the microstructure consisted of a very fine, compact, and homogenous amorphous structure. X-ray analysis indicated that there was considerable deviation between the Si/Ca ratios for the hydrated product.

1. Introduction

Understanding the material structure of new materials at sub-micro scale, can lead to improved development of such materials for the construction and building industries. In order to examine properties of these materials at micro (or Nano) scale, it is essential to observe their morphology, particle size, chemical compositions, and physical characteristics (Sharif, 2016). Nowadays, nano characterization of novel construction materials has become a significant field of research (Sharif, 2016). In particular, the nanoscopy techniques utilizing electron microscopes are the most commonly used methods for cement-based materials.

The electron microscope is a microscope that uses a beam of high voltage electron to create an image of the sample. Electron microscopes are typically used to examine the micro-structure of a wide range of biological, inorganic, metallic, crystals, polymers, or cementitious materials. By utilizing electromagnetic and/or electrostatic lenses to control path of the electrons, they enable the observation of much smaller objects in finer details. For research related to cement-based building materials, currently, SEM has been heavily used instrument for better understanding of the materials' composition, morphology, topography, and also for obtaining crystallographic information. Despite the fact that combination of higher magnification, larger depth of field, and greater resolution makes SEM one of the most powerful tools in research areas and industries dealing with construction materials (Sharif, 2016), yet there are certain limitations in using SEM for investigating materials' properties especially at the atomic level when compared to TEM, which allows an evaluation of the internal structure and spatial distribution of the various phases. In high resolution, the TEM imaging capability allows the instrument's operator to observe fine details (Sharif, 2016). The current TEM systems can inspect in atomic level, which is in the range of 1 nm or less as compared to the resolution of SEM which is about tens of nm for common materials. Also, TEM can identify many characteristics of the sample, such as morphology, crystallization, stress, or even magnetic domains (holography) but common SEM only scan a specimen surface which mainly provides information about its morphology.

In contrast to TEM, the specimen preparation of SEM is much simpler. Many materials can be directly loaded in SEM for inspection and some insulating materials require an additional coating. On the other hand, TEM sample preparation is a challenging task as specimens need to be thinned to thickness of 100 nm or less. However, the complex multiphase nature of hydration products in cementitious materials makes the preparation of specimens thin enough, for electron penetration and TEM examination, far from trivial (Richardson and Groves, 1993). The thinning procedure is very time consuming and it can be

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https://doi.org/10.1016/j.micron.2018.01.007
Received 31 October 2017; Received in revised form 17 January 2018; Accepted 17 January 2018
Available online 31 January 2018
0968-4328/

done by mechanical breakup and dispersion of the solid (Grudemo, 1964; Lachowski and Diamond, 1983; Lachowski et al., 1980, 1981), replication of fracture surface (Ciach et al., 1971), mechanical thinning (Jennings and Pratt, 1980; Taylor et al., 1985) or abrasive and ion-beam milling (Card et al., 1980; Dalgleish and Ibe, 1981; Dalgleish et al., 1980; Groves and Rodger, 1989; Groves et al., 1986; Jennings et al., 1981; Tiegs, 1975). In the past few years, there has been an upward trend in the use of the Focused Ion Beam (FIB) system which is also adopted in the present work to fabricate a specimen with consistent thickness for TEM examination. By utilizing ion-beam thinning, among other techniques, Jennings et al. (Jennings et al., 1981) could obtain information on the morphology of hydrated Tri-calcium Silicate (C_3S) pastes. Dalgleish and Ibe (Dalgleish and Ibe, 1981) also performed some qualitative analyses of Portland cement pastes thinned by ion-beam milling tool. Groves and co-workers (Groves and Rodger, 1989; Groves et al., 1986) have obtained the thinning procedure of hardened cement pastes using ion-beam milling. Through ion-beam thinning process, the possibility of developing artificial defects during the specimen preparation stage must be wisely considered. The drying impact of the vacuum of the ion-beam thinning apparatus and carbon evaporation chamber is inevitable, as the microscope also operates at high vacuum, it must be realized that any observed morphologies relate to a dry state (Richardson and Groves, 1993).

In previous studies, TEM has been used to observe structures of Di-calcium Silicate (C_2S) and Tri-calcium Silicate (C_3S) at sub-micro scale and examine cement hydration products in the form of dispersed particles or crushed specimens (Card et al., 1980; Grudemo, 1964; Grutzeck and Roy, 1969; Lachowski et al., 1980, 1981). TEM has also been operated to identify both inner and outer product regions of the C-S-H phase. The hydration of dispersed cement fragments has been imaged in an environmental cell by high-voltage TEM (Double et al., 1978), but all these previous studies have not considered the fact that the cement particle is typically too thick to enable its internal structures to be fully observed under TEM. As mentioned by Jennings et al. (Jennings et al., 1981), the abovementioned techniques have limitations in terms of loss of spatial relationships and limitation to a fracture path, respectively. This drawback was overcome with ion-beam milling by Javelas et al. (Javelas et al., 1974) on mature mortars and later by Dalgeish et al. (Dalgleish and Ibe, 1981) on mature cement pastes. Furthermore, TEM has been extensively used by Groves (Groves, 1986; Groves et al., 1986), Henderson (Henderson and Bailey, 1988), Rodger (Rodger and Groves, 1989) and Richardson (Richardson, 1999, 2002, 2004, Richardson and Groves, 1992, 1993). These studies have generally focused on both fresh and mature cementitious materials, hydrated for 2 h or more. Many of the main features and hydration products in a mature ordinary Portland cement (OPC) paste were identified by Rodger and Groves using TEM with microanalysis (Rodger and Groves, 1989). Over a range of Ground Granulated Blast-furnace Slag (GGBS) incorporated with OPCGGBS/OPC, a linear relationship has been observed between an increase in the R/Ca ratio (where R is a trivalent cation, mainly Al_3) and an increase in the Si/Ca ratio (Richardson and Groves, 1992, 1993). Through TEM, early age hydration product shells around cement grains were also studied by Gallucci et al. (Gallucci et al., 2010). In their results, the Ca/Si ratio of C-S-H gel was determined to be 2.8–3.5, which is contrary to findings of other previous studies. Plank et al. (Plank et al., 2006) investigated the intercalation product, composed of AFt and AFm with organic polycarboxylate (PC) polymers using TEM. Its raw material was pure mineral and the intercalation product was synthesized in specified condition.

The size distributions, as a factor to be considered for nanomaterials, can be envisaged with TEM (Borchert et al., 2005; Lin et al., 2008; Sun et al., 2005; Zhang et al., 2004; Ziel et al., 2008). Hou et al. (Hou et al., 2015) studied the effects of colloidal nano-SiO_2 (CNS) with a mean particle size of 20 nm and its precursor, tetraethoxysilane (TEOS), on the transport properties of hardened cement pastes with various *w/c* ratios. TEM morphology micrograph in this study indicated that CNS particles are generally round in shape and well-dispersed, however, agglomeration are also observed. Monitoring the interaction between various components of a mixture can be also clearly achieved by TEM. For instance, the microstructure of fly ash binders incorporated by cement kiln dust (CKD), a by-product of the cement industry, was investigated under a TEM (Chaunsali and Peethamparan, 2013). Through TEM work, the morphology of calcium alumino-silicate hydrate (C-A-S-H) gel present in the CKD-based fly ash binders, was evidently observed to be fibrillar type. To identify crystalline phases for cement paste at an age of 90 days, Ramezanianpour et al. (Ramezanianpour et al., 2014) used TEM in bright field mode. In their TEM micrographs, hexagonal portlandite ($Ca(OH)_2$) crystalline cubes and aragonite ($CaCO_3$) was observed. Recently, there is an upward trend among physical and biological science disciplines to use TEM for real-time observations of materials interactions in their native fluid environment (Xin et al., 2013). For the in-situ transformation observation, Xin et al. (Xin et al., 2013) embedded their sample inside a micro-fabricated cell with electron transparent membranes in order to contain the fluid in the high vacuum environment of the microscope.

Table 1
Physical properties of CRM.

Color	Gray
Texture	Powder
Particle size	40–150 μm
Bulk density	1.2–1.5 g/cm^3
pH	13 (when mixed with water)
Solids	100%

With the development of SEM and TEM, the associate technique of Scanning Transmission Electron Microscopy (STEM) was first described in 1938 by Manfred von Ardenne and later re-investigated at University of Chicago by Crewe et al. (Crewe et al., 1969) with advancement of the field emission gun and adding a high-quality objective lens. Using annular dark-field imaging, Crewe was able to image single heavy atoms on thin carbon substrates (Crewe et al., 1970). Later, the first attempt on cementitious materials at early age was made using STEM to observe the formation of separated shells around reacting cement grains in samples as young as 5 h (Scrivener, 1984; Scrivener and Pratt, 1983). Mixtures of mono-phased grains of C_3S, C_3A and hemi-hydrate were also studied using STEM in Scrivener and Pratt's work (Scrivener and Pratt, 1984). At 1-day of hydration, they noticed gaps of up to 10 μm between C_3A grains and their hydration shells while there was a close contact between the C_3S grains and hydration products. This difference in behavior between cement and mixtures of pure phases indicates that the hydration process is influenced by the anhydrous phases within the cement grains (Scrivener and Pratt, 1984). Although, STEM and SEM have been widely used to examine and review the micro-level structure of cement-based materials for building and construction industries, the manufacturing procedures and quantitative techniques for microscopic level investigation using STEM have not been reported in detail in any present-day literature. Hence, the authors have attempted to investigate the microstructure of CRM that contribute to bond cracks together to identify its morphology, chemical compositions, and obtain crystallographic information of this material.

The objectives of the current study are to provide better understanding about fabrication and examination of a cement-based repair material at sub-micro scale as well as detailed characterization of its morphology, composition and structure using one of the highest resolution STEHM in the world as the main tool of investigation. Through this paper, the fabrication process and STEHM analyses of ion-thinned CRM sample, cured and activated for 7-days by spraying water, are also explained in Section 2, followed by obtained results and discussion presented in Section 3. This study is expected to be of significant value in the investigation of the CRMs' nanostructure and the composition of