Micron 68 (2015) 54–58

Contents lists available at ScienceDirect

Micron

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

Characterization of multi-scale porous structure of fly ash/phosphate geopolymer hollow sphere structures: From submillimeter to nano-scale

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ARTICLE INFO

Article history:
Received 9 July 2014
Received in revised form 9 September 2014
Accepted 15 September 2014

Keywords:
Porous materials
Hollow sphere structures
Multi-scale porous structure
Nano-pores
Transmission electron microscopy

ABSTRACT

In the present work, the porous structure of fly ash/phosphate geopolymer hollow sphere structures (FPGHSS), prepared by pre-bonding and curing technology, has been characterized by multi-resolution methods from sub-millimeter to nano-scale. Micro-CT and confocal microscopy could provide the macroscopic distribution of porous structure on sub-millimeter scale, and hollow fly ashes with sphere shape and several sub-millimeter open cells with irregular shape were identified. SEM is more suitable to illustrate the distribution of micro-sized open and closed cells, and it was found that the open cells of FPGHSS were mainly formed in the interstitial porosity between fly ashes. Mercury porosimeter measurement showed that the micro-sized open cell of FPGHSS demonstrated a normal/bimodal distribution, and the peaks of pore size distribution were mainly around 100 and 10 μm. TEM observation revealed that the phosphate geopolymer was mainly composed of the porous area with nano-pores and dense areas, which were amorphous Al–O–P phase and α-Al_2O_3 respectively. The pore size of nano-pores demonstrated a quasi-normal distribution from about 10 to 100 nm. Therefore, detailed information of the porous structure of FPGHSS could be revealed using multiple methods.

1. Introduction

Hollow sphere structures (HSS) are a new group of porous materials that could meet both multi-functional and structural requirements (Öchsner and Augustin, 2009). It is well known that the functional (Janousch et al., 2014; Solórzano et al., 2009) and mechanical properties (Wiest et al., 2014) of porous materials are highly related to their porous structure. Recently, great deal efforts have been paid on the complete characterization of the porous structure on length scale from micrometer to nanometer (Tariq et al., 2011). However, the fully understand of the multi-scale porous structure of HSS has been rarely reported (Öchsner, 2009).

Several methods, such as microscopic methods and X-ray microtomography (Bera et al., 2011; Shanti et al., 2014), have been adopted to analyze the micro-sized porous structure. It should be noted that porous structure on the scale of micrometer could be characterized by confocal microscopy and scanning electron microscopy (SEM) (Menéndez et al., 2001; Zankel et al., 2014). Further, three-dimensional views of the porous structure of aluminosilicate geopolymer gel on sub-micron scale were studied by hard X-ray nanotomography (Provis et al., 2011). However, investigation of porous structure on nano-scale has been rarely reported due to the resolution limitation of confocal microscopy, SEM and X-ray tomography. Transmission electron microscope (TEM) is an effective method to observe the microstructure on nano-scale (Tariq et al., 2011). However, it is a high challenge to prepare porous samples for TEM observation (Provis et al., 2011).

In the present work, the fly ash/phosphate geopolymer hollow sphere structures (FPGHSS) were prepared by pre-bonding and curing technology. The multi-scale porous structures of FPGHSS have been analyzed by multi-resolution methods from sub-millimeter to nanoscale, including X-ray microtomography, confocal microscope, SEM and TEM. Quantitative mercury intrusion method was introduced to measure the pore size distribution of micro- and nano-open cell, and the TEM was used to characterize the nanoporous structure.

2. Materials and methods

In the present work, F-grade fly ash (Yaomeng power plant, Henan province, China), with size distribution of approximate 150–230 μm, was chosen as hollow sphere, and phosphate

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http://dx.doi.org/10.1016/j.micron.2014.09.005
0968-4328/

geopolymer (PG) (Institute of Petrochemistry, Heilongjiang Academy of Sciences, China) was used as inorganic adhesive. FPGHSS were prepared by pre-bonding and curing process. The mass ratio of fly ash/APG was 11:9, and then they were mixed uniformly by mechanical stirring; further the preform was produced by "pre-bonding". Finally, the preform was cured at 200 °C to achieve HSS. It should be noted that the nano-pores in PG, which are generated during the curing process, are slightly affected by the structure of fly ashes. Therefore, the fly ashes were grinded to sub-micron sized powder, and then mingled with inorganic adhesive. Furthermore, after pre-bonding and curing process, dense fly ash/phosphate geopolymer composites were prepared for nano-pore observation.

The macroscopic porous structure of FPGHSS on sub-millimeter scale was characterized by X-ray microtomography (micro-CT) (Y.CT Precision S, YXLON International GmbH, Germany), with spatial resolution of 44 μm, and the specimen size is ∅6 mm × 10 mm. A series of 2D images, consisting of 720 images, were acquired as the sample rotated stepwise through 360°. Furthermore, the tomographic reconstruction was carried out using the ImageJ software package (version 1.48), and the median filtering was applied to reduce image noise. The porous structure of FPGHSS on hundreds microns was observed by confocal scanning laser microscopy (CSLM, OLYMPUS LEXT OLS4100, Japan), and the pore size distribution of closed cell was measured by standard 2D optical microscopy method. The porous structure on the length scale of micrometer was observed by scanning electron microscopy (SEM) (Quanta 200FEG, FEI, USA). Moreover, the pore size distribution of open cell was characterized by mercury porosimetry (Autopore IV 9500, Micromeritics Instrument, USA), according to ISO 15901-1:2005. The samples for TEM observation were firstly polished to be 60 μm in thickness, and then thinned by ion beam thinning (GATAN-691 Ionic Reduced Imager, GATAN, USA). The nano-porous structure of FPGHSS was characterized by field emission transmission electron microscopy (Tecnai G2 F30, FEI, USA).

3. Results and discussion

3.1. Sub-millimeter scale porous structure

The macro-porous structure of HSS characterized by micro-CT is shown in Fig. 1. It is obvious that the porous structure on sub-millimeter scale could be well identified by micro-CT since the resolution of the micro-CT used in the present work was about 44 μm. Hollow fly ashes with nearly sphere shape and sub-millimeter pore size, which have been marked as closed cells by red circles in Fig. 1, were distributed uniformly in FPGHSS, as shown in the reconstructed orthogonal micro-CT slices (Fig. 1a). Moreover, as shown in Fig. 1b and c, it is obviously that the hollow fly ashes were randomly packed, which is beneficial for the mechanical performance of HSS (Lim et al., 2002), and helpful for the calculation of acoustical properties based on models (Fallet et al., 2013). Furthermore, several sub-millimeter open cells with irregular shape (marked as green dotted lines in Fig. 1) could also be found in the FPGHSS. However, due to the resolution limitation of the micro-CT, the porous structure of micro-sized open cell of FPGHSS could not be clearly identified. In this work, it should be noted that the micro-CT could provide a macroscopic view of porous structure of FPGHSS on sub-millimeter scale, which is significant to the nondestructive examination of macroscopic defects (Bull et al., 2013).

The 3D porous structure of HSS observed by CSLM is shown in Fig. 2a and b. The 3D porous structure was well reconstructed with detailed depth information (Fig. 2b), by which the closed cell with sphere shape could be clearly observed. Based on the results observed by the standard 2D optical microscopy (Fig. 2c), the pore size distribution of closed cell of FPGHSS on sub-millimeter scale, which is shown in Fig. 2d, was determined via measuring hundreds of 2D sections. It is interesting to note that the pore size distribution of closed cell of FPGHSS, which was mainly from 140 to 220 μm, demonstrated a bimodal distribution, and the peak values of pore size distribution were about 180–190 μm and 210–220 μm, respectively. However, it is difficult to identify the porous structure of open cell and distinguish the fly ashes from each other through optical observation (Fig. 2a), which might be due to the poor light reflection of fly ash and PG.

3.2. Micro-scale porous structure

The micron porous structure of FPGHSS observed by SEM is shown in Fig. 3a–c. It can be seen that the open cell of FPGHSS (marked by green dotted circles as shown in Fig. 3a) was mainly formed in the interstitial porosity between fly ashes. Furthermore, irregular open cells with pore size of about 100 μm, which are similar to the open porous structure in conventional HSS (Cochran, 1998), were illustrated in Fig. 3b. Moreover, it is interesting to note that micro-sized open cells (about 10 μm), which were generated in the gaps between oxides (curing agent) of PG (Wagh, 2004), were observed in the porous PG coating (Fig. 3c).

The pore size distribution of micro-sized open cell of FPGHSS measured by mercury porosimeter is shown in Fig. 3d. It is obvious

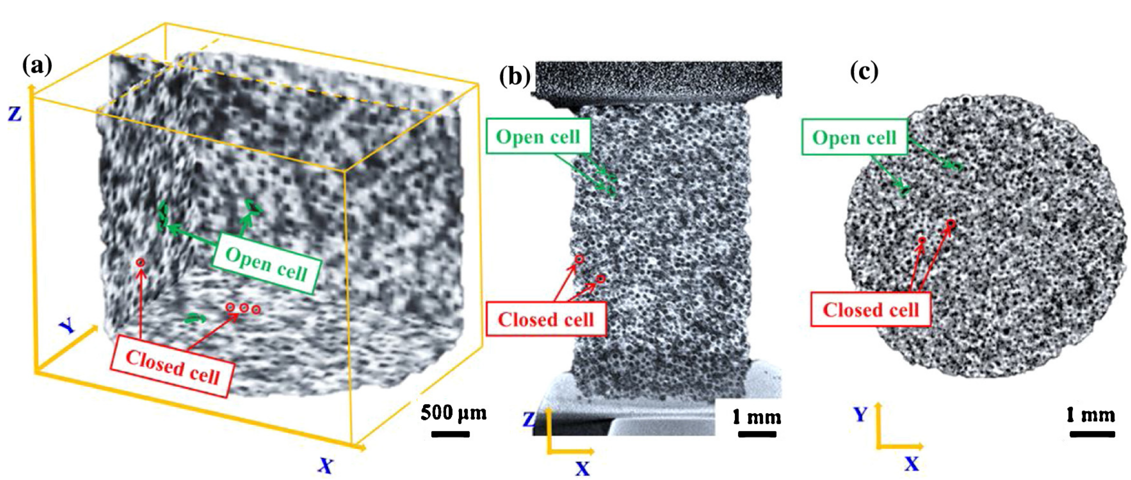

Fig. 1. Porous structure of FPGHSS characterized by micro-CT with resolution of 44 μm: (a) reconstructed orthogonal CT slices; (b) reconstructed longitudinal CT slice and (c) reconstructed cross-sectional CT slice. (For interpretation of the references to color in this sentence, the reader is referred to the web version of the article.)