



Contents lists available at ScienceDirect

Advanced Powder Technology

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

Original Research Paper

Eggshell biomaterial: Characterization of nanophase and polymorphs after mechanical activation

Matej Baláž^{a,*}, Anna Zorkovská^a, Martin Fabián^a, Vladimír Girman^b, Jaroslav Briančin^a^a Department of Mechanochemistry, Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, 04001 Košice, Slovakia^b Institute of Physics, P.J. Šafárik University, Park Angelinum 9, 041 54 Košice, Slovakia

ARTICLE INFO

Article history:

Received 1 December 2014

Received in revised form 20 May 2015

Accepted 11 September 2015

Available online xxxx

Keywords:

Eggshell

Mechanical activation

Nanophase

Phase transformation

Mesopores

Microstructural characterization

ABSTRACT

Eggshell biomaterial is generally considered waste, however it can be applied in various areas of research due to its unique properties. In this study, the two-phase eggshell nanopowder was prepared by the process of mechanical activation in a planetary ball mill. The phase transformation from calcite, which is the main component of the ES, into aragonite was studied in detail and the properties of milled eggshell were pursued. The effect of mechanical activation was investigated by means of X-ray diffraction, Fourier-transform infrared spectroscopy, nitrogen adsorption, grain size analysis, scanning and transmission electron microscopy and energy-dispersive X-ray spectroscopy. The calcite–aragonite phase transformation was confirmed with the conclusion that after 360 min of milling, 58% aragonite is present in the system. The presence of nanoparticles containing mesopores was evidenced.

© 2015 Published by Elsevier B.V. on behalf of The Society of Powder Technology Japan. All rights reserved.

1. Introduction

The eggshell (ES) is one of the most common biomaterials in nature. It is a very interesting material for potential waste treatment, because it is a by-product in food industry and after the production of eggs is considered waste. The ES together with the eggshell membrane (ESM), represents 11% of the total weight of the egg and its main component is calcite CaCO_3 (94%). The residual components include MgCO_3 (1%), $\text{Ca}_3(\text{PO}_4)_2$ (1%) and organic matter (4%) [1]. It exhibits a unique microstructure [2,3] and has very interesting application potential [4,5]. Despite its abundance, it is not adequately used on the industrial scale. The particular areas include its use as a fertilizer and soil conditioner [6], as a sorbent of heavy metals [7,8] or dyes [9], as a source of calcium for the synthesis of hydroxyapatite [10], as a source of calcium oxide for the sorption of CO_2 [11], or as a precursor for composite materials used further in various fields [12,13]. If the eggshell biomaterial is nano-sized, its application potential broadens [14,15]. The industrial ES waste contains also ESM, which is suitable for wide palette of applications too [16]. The treatment of ES by various techniques can broaden its application spectrum even more. One of such approaches is the mechanochemical one [17,18].

Mechanochemistry represents an excellent tool for the synthesis of nanoparticles [19,20]. Its particular area, the mechanical activation (MA), makes it possible to decrease the particle size of bulk materials dramatically [21,22]. By applying the appropriate experimental conditions, it is possible to diminish the particles into the nano-region, which significantly increases the application potential of the treated materials [19]. This approach is attractive also from the environmental point of view. The positive influence of MA on the properties of many natural materials was reported in literature [23,24]. This applies also to eggshell biomaterial [17,25,26].

As was already stated, the main component of the ES is calcite with trigonal crystal structure. According to literature, it is prone to undergo the phase transformation into orthorhombic aragonite and vice versa [27–34]. By the investigation of the MA of pure calcite, it was documented that it turns into the orthorhombic aragonite, if proper milling conditions are applied [27–29], mainly due to the fact that the latter is stable at high pressures and exhibits higher density ($\rho_{\text{calcite}} = 2.71 \text{ g cm}^{-3}$, $\rho_{\text{aragonite}} = 2.94 \text{ g cm}^{-3}$). The total conversion from one phase to another was not observed and the ratio between calcite and aragonite in the equilibrium state was approximately 30:70. A similar result was obtained when the milling procedure started from pure aragonite [27]. However, in the case when the milling process was not so intensive, the transformation was not observed [35]. The eggshell material is different from pure calcite and, as was documented in more papers,

* Corresponding author.

E-mail addresses: balazm@saske.sk (M. Baláž), zorkovska@saske.sk (A. Zorkovská), fabianm@saske.sk (M. Fabián), vladimir.girman@upjs.sk (V. Girman), briancin@saske.sk (J. Briančin).

some authors observed the transformation [17], while some did not [36]. The presence of the ESM in the system could also influence this transformation. It is necessary to clarify this issue.

As it was outlined in previous paragraphs, the calcite–aragonite nanophase transformations in the ES are not properly elucidated. Therefore, the detailed characterization of this material during the process of MA is necessary. Within this work, the effect of MA on the eggshell material is deeply investigated, with the focus on the calcite–aragonite phase transformation and the phenomena accompanying the process.

2. Experimental

2.1. Materials

The ES containing ESM was provided by local dining room in Košice. Almost in all samples, the ESM was separated from the ES (see Section 2.2).

2.2. Separation of eggshell membrane

The ESM was separated from the ES in case of all samples except ES+MEM (see Table 1 below). The separation was accomplished by boiling the ES in 0.03 M HCl for 10 min, subsequent cooling down and stabilizing in distilled water for one hour. As a result of this procedure, the ESM separated itself from the ES and it was possible to collect pure ES mechanically. Afterwards, it was dried on air and crushed in a mixer (the crushing procedure was applied also for ES+MEM sample).

2.3. Mechanical activation (MA)

Table 1 gives an overview of the sample labeling, according to the entire preparation process, including the mechanical activation. Fig. 1 schematically depicts the different modifications of the preparation process, including the operations carried out prior to MA.

The samples prepared by the procedure described above were either pre-milled (all samples except ESR), or directly used for MA (ESR). The pre-milling was conducted in a Pulverisette 6 planetary ball mill (Fritsch, Germany), in order to obtain powder with particles smaller than 160 μm , which was then used as an input for the mechanical activation experiments.

MA was performed by milling in the same mill as was used in case of pre-milling. The following milling conditions were used: mass of sample (ES0) – 5 g, loading of the milling media – 50 tungsten carbide balls of 10 mm diameter, volume of the milling chamber – 250 cm^3 , rotation speed of the planet carrier – 500 rpm, milling time 0–360 min, atmosphere – air. For all samples except ESR, new 5 g of non-treated ES were utilized and the mill was not opened until the end of the experiment. The milling was stopped after each 15 min of milling, after which 10 min break followed.

In the case of milling of ESR240 sample, the same milling conditions were applied, except the fact that 10 g of ESR sample was used and that the mill was opened in pre-determined intervals (exactly after 1, 2, 3, 5, 30, 60, 90, 120, 130, 140, 150, 160, 180, 200 and 220 min), in order to collect 0.5 g of the milled powder for the XRD analysis.

2.4. X-ray diffractometry (XRD)

The process of the MA was monitored by XRD, using a D8 Advance diffractometer (Bruker, Germany) equipped with Cu $K\alpha$ radiation (40 kV/40 mA), secondary graphite monochromator and

Table 1

The overview of the studied samples according to the preparation process.

Sample abbreviation	Mechanical activation (min)	Presence of ESM	Opening of the mill	Pre-milling
ESR	–	No	–	No
ES0	–	No	No	Yes
ES1	1	No	No	Yes
ES3	3	No	No	Yes
ES5	5	No	No	Yes
ES15	15	No	No	Yes
ES30	30	No	No	Yes
ES45	45	No	No	Yes
ES60	60	No	No	Yes
ES120	120	No	No	Yes
ES180	180	No	No	Yes
ES240	240	No	No	Yes
ES300	300	No	No	Yes
ES360	360	No	No	Yes
ES+MEM	240	Yes	No	Yes
ESR240	240	No	Yes	No

scintillation detector. The powder diffraction patterns have been obtained with steps 0.02° and fixed counting time 9 s/step. For the data treatment and analysis the commercial Bruker processing tools have been used, concretely, the Diffrac plus Eva for the phase identification and the Diffrac plus Topas for the Rietveld analysis and microstructure characterization. The peaks corresponding to calcite and aragonite were assigned to the phases according to JCPDS-PDF2 database.

2.5. Infrared spectroscopy

The infrared spectra in the frequency range 4000–650 cm^{-1} were obtained by using a FTIR spectrometer Tensor 29 (Bruker, Germany) using the ATR method.

2.6. Specific surface area

The specific surface area was determined by the low-temperature nitrogen adsorption method using a NOVA 1200e Surface Area & Pore Size Analyzer (Quantachrome Instruments, United Kingdom). The values were calculated using BET theory. The complete nitrogen adsorption isotherms were measured and the pore size distribution was calculated using Barret–Joyner–Halenda (BJH) method. For calculations, including the ones for total pore volumes, average pore radii and maximum amount of adsorbed nitrogen, Quantachrome™ NovaWin software was utilized.

2.7. Grain size analysis

The grain size in a micrometer range was determined using a Sympatec Grain Size Analyzer with HELOS laser diffraction sensor (Sympatec, Germany) in a suspension cell (CLCELL) under the following conditions: dispersant – H_2O , anti-agglomerant additive – sodium diphosphate decahydrate $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ (0.1 M), sonification time – 60 s, stirring rate – 60, measuring time – 10 s.

2.8. Scanning electron microscopy and energy-dispersive X-ray spectroscopy

SEM images of the samples were recorded by the utilization of MIRA3 FE-SEM microscope (TESCAN, Czech Republic) equipped with EDX detector (Oxford Instrument, United Kingdom).

Download English Version:

<https://daneshyari.com/en/article/10260315>

Download Persian Version:

<https://daneshyari.com/article/10260315>

[Daneshyari.com](https://daneshyari.com)