HIGH-ENERGY MILLING INDUCED CALCITE TO ARAGONITE TRANSFORMATION IN EGGSHELL

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Abstract

Eggshell biomaterial has been mechanically activated in a high-energy mill in air for increasing time (15 – 960 min). X-ray diffraction study of the milling products has revealed an extensive and fast calcite-to-aragonite transformation. The volume fraction of the aragonite phase reached maximum (~65%) after 240 min. of milling, the mechano-chemical equilibrium between phases was established after 960 min.

Introduction

Eggshell is one of the most commonly occurring biomaterial in nature that shows unique structure and properties, nevertheless, it is mostly discarded as a waste [1]. The eggshell structure, composed predominantly of calcite (94%), calcium phosphate (1%), magnesium carbonate (1%), and of some organic matter (4%), is very sophisticated: following the most recent studies [2], it is built of three layers with entirely different morphologies, all on submicron- to nanoscales. Particularly, there is a surface layer with nano-rods and submicron spheres outside, the so-called palisade layer beneath with rhombohedral cleavage, and finally, there is a lamellar mammillary layer from the inner surface. The inner layers are dominated by pores of diameter ~250 nm. The high degree of porosity suggests the exploitation of eggshell in waste treatment, for possible absorption of heavy metal contamination, gas sequestration, etc.

Mechanical activation (milling) is an often used tool to enhance or modify the materials properties and reactivity [3]. The motivation of the present study was to enhance the capability of eggshell to absorb heavy metal contamination from solutions, by increasing the total surface area via high-energy milling. XRD study of the milling products revealed an extensive and fast calcite-to-aragonite transformation during the milling.

Experimental techniques

Eggshell biomaterial was mechanically activated in a planetary mill Pulverisette 6 (Fritsch, Germany) under the following conditions: loading of the mill with 50 tungsten carbide balls of 10 mm diameter, powder/ball weight ratio of 1/70, rotation speed of the planet carrier 500 rpm, milling time 15-960 min, working atmosphere – air.

Microphotographs were taken using the FE-SEM LEO 1550 scanning electron microscope.

X-ray powder diffraction data were collected over an angular range 15<2Theta<115° with steps 0.1 and fixed counting time of 20s per step, using a D8 Advance diffractometer (Bruker, Germany), working with Cu K radiation (40 kV/40 mA) and a scintillation point detector, arranged in Bragg-Brentano geometry. Fixed divergence slit of 0.3 mm width and receiving slit of 0.1 mm width were used and for background attenuation a secondary graphite monochromator was employed. Both the primary and secondary optics were equipped with Soller slits (2.5°). The diffraction patterns were treated with the MAUD and Diffrac^{plus} Topas software. Full profile Rietveld analysis has been carried out using the Pseudo-Voigt peak shape function, the corresponding parameters together with the structure parameters have been refined.

Results

Calcite crystals are trigonal-rhombohedral. Aragonite, as a high-pressure orthorhombic polymorph of calcite is known to form under certain pressure and temperature conditions [4] and under milling as well [5]. It is also known that me-

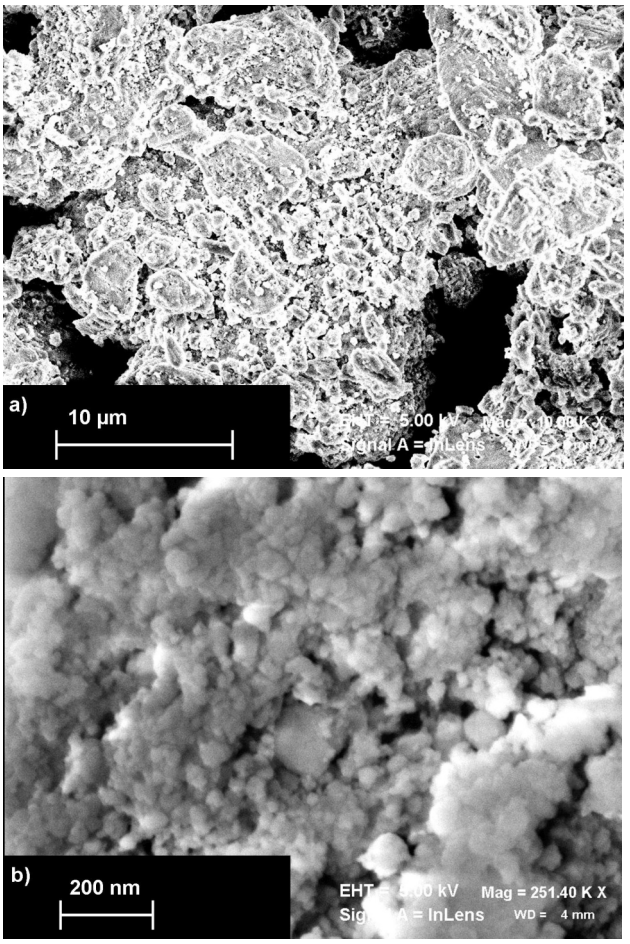

Figure 1. Scanning electron microphotographs of a) non-milled eggshell and b) of the samples milled for 240 min.

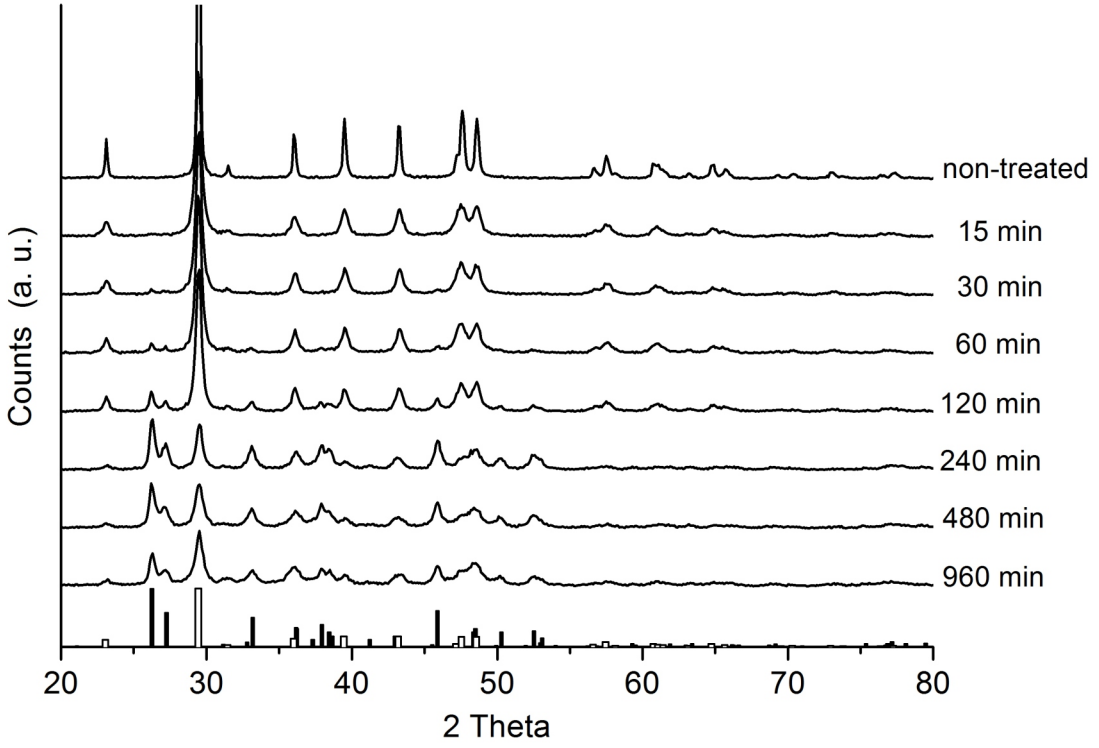

Figure 2. XRD patterns of high-energy milled eggshell. Duration of milling and the correspondent patterns of 85-1108-calcite (□) and 71-2392-aragonite (■) are indicated in the graph, according to the ICDD-PDF2 database.

chanical activation frequently leads to polymorphism. The high local pressures at the contact surface of the mechanically activated particles, as well as the presence of volume defects are responsible for the phase transformations [6]. Nevertheless, the feasibility of the calcite-to-aragonite transformation process, its rate and extent in the eggshell has not been studied yet.

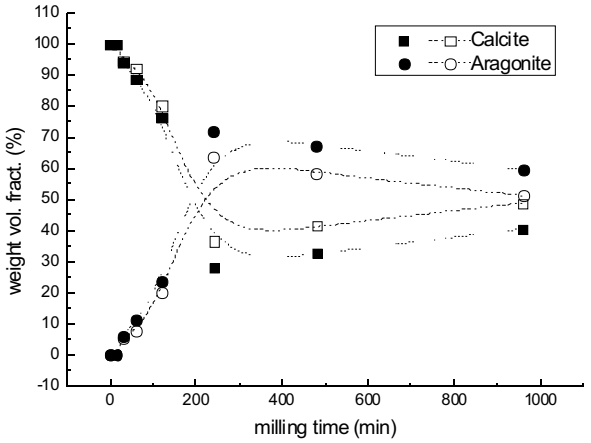

Figure 3. Evolution of the calcite and aragonite volume fraction during the milling process. Full and hollow symbols were obtained by analysis of spectra using the MAUD and Diffrac^{plus} Topas softwares, respectively.

According to our study, the calcite, which represents almost 100% of volume fraction in the original eggshell material, starts to transform into aragonite at the early stage of milling, after 15 min. (Fig. 2), what is much shorter time than in case of mineral calcite [5]. The porosity of the eggshell material and the large initial total surface are surely the attributes that facilitate the transformation process.

The evolution of diffraction patterns with milling time (Fig. 2) reveals a considerable line broadening which takes place mainly during the first 15 minutes and is related to the reduction of crystallite size as well as to the changes in structure. Our analysis has shown that the lattice parameters of the eggshell calcite are close to those of the ideal structure and change only slightly during the milling, while the as-formed aragonite has more deformed crystal structure, with lattice parameters considerably larger than for the ideal crystal, the maximum deviation reaches 1%. This fact should be related to the strong strain, which accompanies the milling process.

Fig. 3 shows the progress of calcite-to-aragonite transformation. The maximum amount of aragonite (65%) is achieved after 240 min. Longer milling probably starts the reverse transformation to calcite to dominate [7], which leads to the decrease of the aragonite amount, and finally, the mechano-chemical equilibrium state is reached after 960 min.

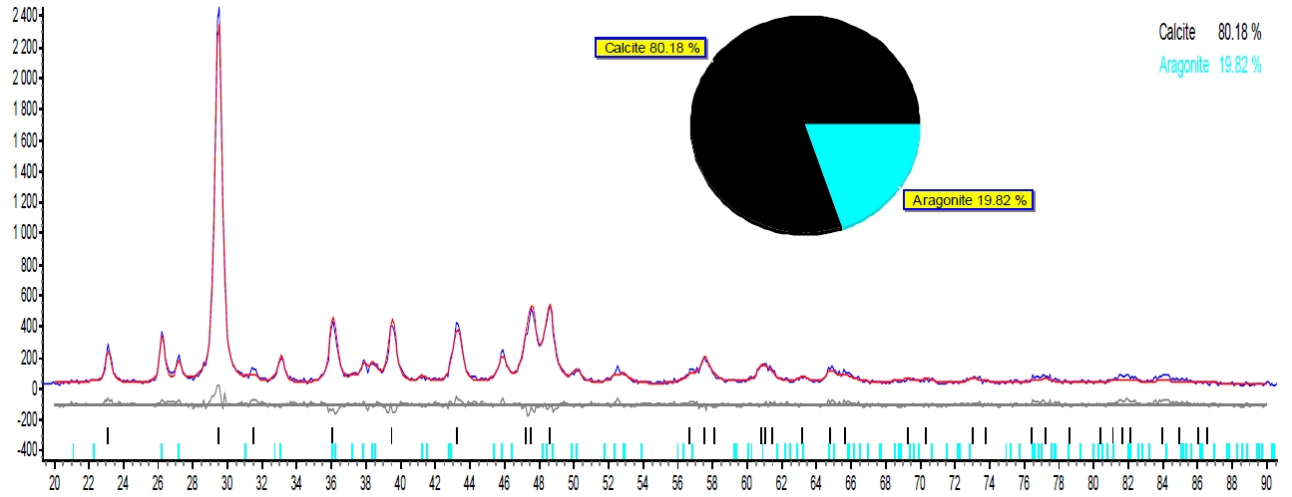

Figure 4. Example of full profile fitting and quantitative analysis of the diffractograms, using the Diffrac^{plus} Topas software. The data of samples milled 120 min. (blue), the fitted spectrum (red), the difference (grey) and the peak positions corresponding to the 85-1108-calcite and 71-2392-aragonite according to the ICDD-PDF2 database are indicated.

Fig. 4 represents an illustration of full profile fitting and quantitative analysis of XRD data, using the Diffrac^{plus} Topas software.

Summary

Mechanically stimulated calcite-to-aragonite transformation has been observed for the first time in eggshell biomaterial during high-energy milling. The transformation has been studied using the powder X-ray diffraction technique. The full profile analysis using the MAUD and Diffrac^{plus} Topas software has revealed fast and extensive transformation. The transformation rate is higher than in case of mineral calcite, probably due to the unique porous structure of the eggshell. The maximum aragonite volume fraction has been achieved after 240 min. and the mechano-chemical equilibrium between the phases has been established after 960 min. of milling.

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