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Ceramics International 30 (2004) 2011–2014

CERAMICS
INTERNATIONAL

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Laminated microstructure of Bivalva shell and research of biomimetic ceramic/polymer composite

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Received 11 December 2003; received in revised form 17 December 2003; accepted 22 December 2003

Abstract

The molluscan shell is a natural ceramic composite with excellent fracture strength and fracture toughness, which are attributed to their unique microstructures. SEM observation on Bivalva shell showed that the shell consists of laminated aragonites and organic layers. There are different shapes and arrangements of aragonites. The higher fracture roughness of this laminated microstructure is analyzed. The laminated microstructure of the shell is used for the biomimetic designs of the ceramic/polymer and ceramic/polymer/fiber composite. Comparison of test of the biomimetic ceramic composite with the original ceramic material shows that the fracture toughness of the biomimetically designed ceramic composite increases markedly than that of the original ceramic material.

Keywords: B. Composite; B. Microstructure; Bivalva shell; Ceramic; Biomimetics; Fracture toughness

1. Introduction

Ceramic materials have high hardness and high temperature resistance, but their fracture toughness is relatively low due to its sensitivity to existing flaws. The main component of mollusc shell is calcium salt so it is thought as a natural ceramic composite. Through it contains 95% $CaCO_3$ in the form of aragonite, the fracture work it can bear can be up to 3000 times that of pure aragoinite [1]. Such a big magnification can be attributed to the microstructure of the shell, suggesting a detailed investigation to the microstructure for the development of promising synthetic ceramic materials [2].

A molluscan shell material is composed of 95–99% crystalline calcite or aragonite (form of calcium carbonate ($CaCO_3$)) and protein film which is used as the binder in varying amount from 0.1 to 5% by weight [3]. A molluscan shell can be divided into three primary sections: periostracum, prismatic, and nacreous layers. The sum of the prismatic and nacreous layers occupies the main structural part of the shell, determining the shape, mechanical strength, and toughness of the shell. The periostracum is the outer layer, consisting mainly of conchiolins. The prismatic layer is the middle layer, consisting mainly of orientated calcitic crystals. The nacreous layer is the inner layer, consisting mainly of orientated aragonite crystals [4]. In nacre, the inorganic aragonite (calcium carbonate) looks like 'brick' and the biopolymer look like 'mortar'. The inorganic 'brick' is 0.4–0.5 μm thick and 5–10 μm wide, the organic 'mortar or adhesive' between the bricks is about 20–30 nm in thickness [3]. The key features of the 'brick' and 'mortar' microstructure were illustrated with fractured surfaces of Pinctada nacre [5]. An important aspect of the study of mollusc shell structures has been the efforts directed at mimicing or duplicating these biological processes [3]. Kessler et al. [6] studied the fracture behavior of the conch shell and presented an approximate fracture mechanics model for describing the fracture mechanism. Wang et al. [7] designed two kinds of high toughness ceramic composites of Si_3N_4/BN based on the analysis on the structure of natural biomaterials.

In this paper, the SEM observation on the microstructures of Bivalva shell is presented. It shows that the shell consists of laminated aragonite and organic layers. It contains many layers, which are parallel to the shell surface but in different

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doi:10.1016/j.ceramint.2003.12.169

orientation. The fracture toughness of the mollusc shell is researched based on the main mechanisms that the fiber-like aragonite plates or sheets are pulled out from their organic matrix. Based on the observed microstructures, two kinds of biomimetic ceramic/epoxy resin composite laminates are fabricated. The impact toughness of these biomimetic laminates is tested and compared with monolithic ceramics. The results show that the impact toughness of the biomimetic composite laminates is markedly larger than that of the monolithic ceramics.

2. SEM observation of the microstructure of Bivalva shell

Structural characteristics vary between species of molluscan shell as well as within the same species, based on such factors as age and the environment in which the mollusc was raised. Therefore, the characteristics discussed here may not represent that of other molluscan shells. The shell used in this study is a Bivalva shell (Unio douglasiae, Fig. 1). It is of fan shape, milk white with brown stripe and about 50 mm in maximal length. The SEM samples were prepared by removing the shell from the mollusc, submerging it in liquid nitrogen for about 2 min and then break it down transversely with a small hammer. The obtained samples are about 10–15 mm. The specimens were then placed on a metal tray using viscid fabric. A 12 nm coat of gold–palladium was made using a sputter coater. These samples were then observed using an Amray KYKY-1000B SEM under the voltage of about 20 kV and with magnifications ranged from 20 to 11,000×. The focus of the observations is the prismatic and the nacreous layers of the shell.

Fig. 1. The Bivalva with fan shape.

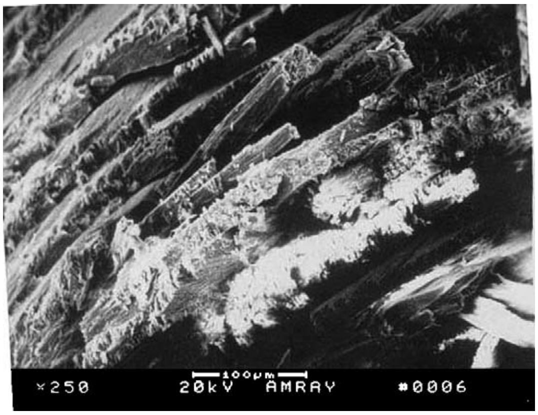

Fig. 2. The curly ‘tile’ of aragonite packed tightly together.

Mollusc shell consists of laminated aragonites (or calcites) and organic layers (collagen). Among the microstructural characteristics, the orientation, shape, and size of the aragonites dominate the mechanical properties of mollusc shell [4], which has been receiving much attention but is still surrounded by controversy. The most widely accepted point of view is that the nacre layer consists of a series of inorganic straight ‘bricks’, and the prismatic layer consists of a series of inorganic ‘lathes’ parallel with each other. These ‘bricks’ or ‘lathes’ are packed tightly together and agglutinated with a biopolymer collagen ‘mortar’ [3,4]. The observed microstructure supports this point of view in most aspects but with slight difference. Instead of straight ‘bricks’, it was found that the aragonites have thin shape. In some places of the shell, a kind of curved and thin aragonite sheet, which looks like a “tile”, can be found (Fig. 2). The sheet with curved shape can increase the interface between the aragonite and the collagen. Fig. 3 shows another aragonite microstructure, the shape of these aragonites look like slats. These “slats” packed tightly together are not completely parallel with each other, which helps increasing the pull-out force. The more careful observation reveals that these aragonite sheets or slats consist of nanoscale aragonite sheets or slats (Figs. 3–6). The combination of multiscale microstructures endows the mollusc shell with excellent mechanical property. The observation also shows that the sheets or lathes of the aragonites at different location have different sizes and shapes. For example, the size of the lathes in the inner layer of the shell is larger and thicker than that in the outer layer of the shell. The size and shape of the lathes corresponds to the stress in that location of the shell. The arrangements of the aragonite sheets and lathes in the shell were also researched. The results

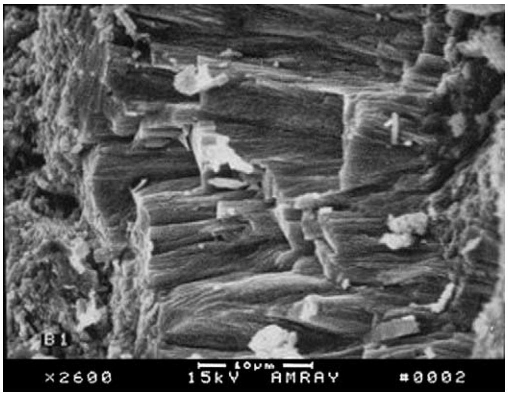

Fig. 3. The ‘slat’ of aragonite packed tightly together.

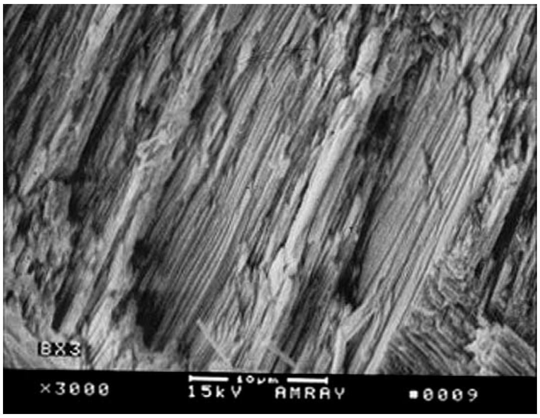

Fig. 4. The “fiber” shape and arrangement of aragonite.

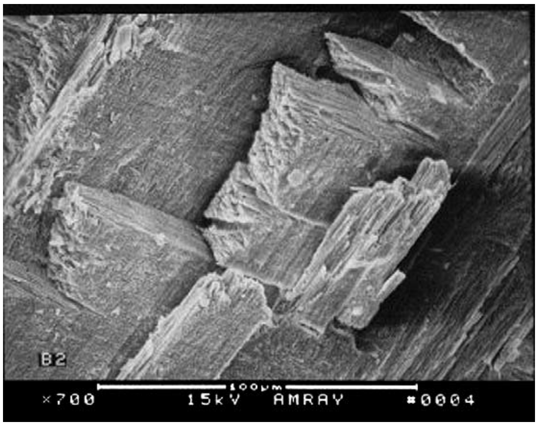

Fig. 5. The aragonite battens with crossed arrangement.

show that there are various aragonite arrangements. These arrangements look like “fiber” layup which include parallel (Fig. 4), crossed (Fig. 5), and inclined ones (Fig. 6). These arrangements of “fiber” may increase the energy dissipated when “fibers” are pulled out from matrix, which may, in turn, increase the fracture toughness of the material.

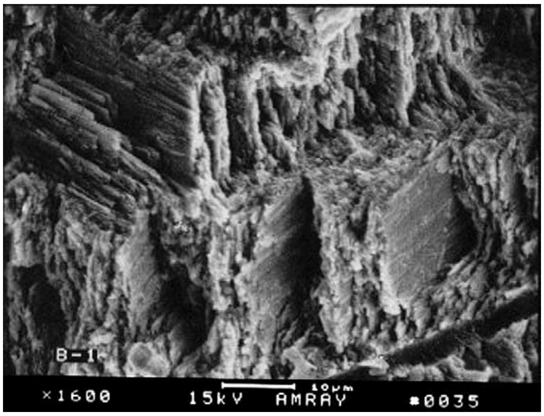

Fig. 6. The aragonite sheets with inclined arrangement.

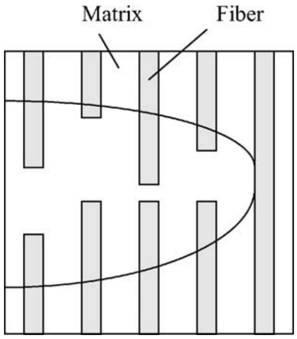

Fig. 7. The sketch of the putout of fibers from matrix.

3. The energy dissipation for pull-out of aragonite from matrix

The aragonite “fiber” observed in the seashell is not common in man-made ceramics. The increase of the energy dissipated when pulling ‘fibers’ out from the matrix is the main mechanism to increase fracture toughness of molluscan shell [5]. Suppose the aragonite “fibers” embedded in the matrix were straight and parallel to the direction of the traction (Fig. 7), the work done by pulling the fibers out from matrix can be estimated with [8]

$$W_{\mathrm{P}} = \frac{V_{\mathrm{f}} \tau_{\mathrm{z}} D^2}{6d} \qquad (1)$$

where W_{P} is the work dissipated, V_{f} and τ_{z} the fiber volume fraction and the shear stress at fiber and matrix interface, D the interval between two lacuna in the fibers [8], which corresponds to the length of pull-out part of a fiber, and d is the diameter of fiber. It can be seen from Eq. (1) that the larger the fiber volume fraction V_{f}, the shear stress at fiber and matrix interface τ_{z} and the interval of two lacuna D, the more the work will be dissipated. The larger the diameter d is, the less the fracture work of the ‘fibers’ will be. It can be illustrates why the volume fraction of the aragonite “fibers” is such large and their size is such small in mollusc shell of higher fracture strength and fracture toughness.

4. Fabrication and impact toughness test of biomimic ceramics/polymer composite

The unique laminated microstructure observed in Unio douglasiae shell was used to design and fabricate biomimetic ceramic composite. Two kinds of biomimetic ceramics/polymer composites were investigated. One is the BN/epoxy resin and the other is BN/EW160A glass/epoxy fabric composite. These materials were selected because of their extensive use in civil and industrial structures. The fabrication of the composite specimens is stated as follows: firstly, BN was produced into sheets of 4 mm thickness, then these sheets were felted with epoxy resin, after that, the laminate was placed in a hot press and the

Table 1
Testing results of ultimate impact toughness, shows a remarkable increase in the impact fracture toughness of the laminated ceramic/polymer specimens with fiber or without fiber compared with that of the monolithic form of the same ceramic specimens

Number of layer	Ultimate impact toughness of laminated ceramics with fibers (10^{-3} J/mm^2)	Ultimate impact toughness of laminated ceramics without fibers (10^{-3} J/mm^2)	Ultimate impact toughness of monolithic ceramics (10^{-3} J/mm^2)
3	4.3	3.4	2.6
4	5.2	4.6	3.2

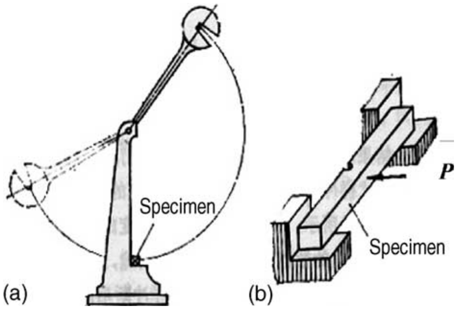

Fig. 8. The sketch of the experiment of the impact fracture toughness.

cured under pressure of 80 MPa at 120 °C for 12 h when the composite laminate was solidified. Then the ceramics/resin composite laminates were machined into the specimens for impact experiment. The fabrication of the BN/EW160A glass/epoxy fabric composite specimens is similar to that of the BN/epoxy resin, the difference is that fiber fabrics were placed between ceramic sheets.

The impact toughness of these specimens was tested with an impact toughness tester. The sketches of the experiment and the specimens are shown in Fig. 8. For comparison, monolithic ceramics with the same size were also fabricated and tested. The impact toughness can be calculated as follows:

$$\alpha_{\mathrm{k}} = \frac{W}{ab} \qquad (1)$$

where W is the energy absorbed by the specimen during impact fracture process, α_{k} the impact fracture toughness, and a and b are the width and the thickness of the working section of the specimens. The impact fracture toughness of the two kinds of biomimetic ceramic composite laminate and the monolithic ceramics are shown in Table 1. It can be seen that the impact fracture toughness of the laminated specimens with BN/epoxy resin has a remarkable increase compared with that of the specimens of monolithic BN, and the impact toughness of the laminated specimens of BN/resin/fiber is the largest in the three kinds of specimens.

5. Conclusions

The SEM observation of Bivalva (Unio douglasiae) shell reveals that the shell is an organic–inorganic composite laminate. The laminated aragonites embedded in proteinaceous matrix and paralleled the surface of the shell. The SEM observation also shows that the laminated aragonites have various sizes and shapes in the shell which include curl aragonite sheets and incompletely parallel slats. These aragonites consist of thinner aragonite sheets or slats. The arrangements of aragonites have also various forms which include parallel, crossed, and inclined ones. The size, shape, and arrangement adopted depend strongly on the state of local stress. The energy dissipated during the fracture of shell and the pulled out of ‘fibers’ of aragonites can illustrate the excellent toughness of molluscan shell. The specimens of two kinds of biomimetic composite laminates were made and tested. The results show that the impact fracture toughness of the specimens of two kinds of the biomimetic ceramic/polymer composite laminates markedly increases compared with that of monolithic ceramics.

Acknowledgements

The authors gratefully acknowledge the financial support to this work from the Natural Science Foundation of China (Grant no. 10272120) and the Science and Technology Commission of Chongqing (Grant no. 6782).

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