Research of Nanostructure of Bivalva Shell

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Keywords: Bivalva shell, nanoscale, ceramic, biocomposite, fracture strength, fracture toughness.

Abstract. Molluscan shells is a natural ceramic composite with excellent fracture strength and fracture toughness, which are attributed to their unique microstructures. Scanning electron microscope (SEM) observation on Bivalva shell showed that the shell consists of laminated aragonite and organic layers. These aragonite and organic layers are provided with the scale and characteristics of nanometer. The effect and function of these nanometer structures were analyzed based on Griffith criterion and energy-dissipation idea. The higher fracture strength and fracture roughness of bionanocomposite-molluscan shell were well explained with nanometer viewpoint.

1. Introduction

Ceramic materials behave high hardness and temperature resistance, but their fracture toughness is relatively low due to its sensitivity to existing flaws. The main component of molluscan shell is calcium salt so its can be can be thought as a natural ceramic composite. Through it contains 95% CaCO₃ in the form of aragonite, the fracture work it can bear can be up to 3000 times that of pure aragonite [1]. Such a big magnification can be attributed to the microstructures of the shell, suggesting a detailed investigation to the microstructures 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 (CaCO₃)) 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 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 ‘sheet’ and the biopolymer look like ‘mortar’. The inorganic ‘sheet’ is 0.4-0.5 μm thick and 5-10 μm wide, the organic ‘mortar or adhesive’ between the sheets is about 20-30nm in thickness [5]. In this paper, The SEM observation to the microstructures of Bivalva shell is presented. It shows that the shell consists of laminated aragonite and organic layers. The observations also show that the laminated aragonite and organic layers possess nanometer scale and characteristics. The high fracture strength and fracture toughness of the shell were analyzed based on Griffith criterion and the energy-dissipation idea. The results show that the high fracture strength of the shell is related to its nanometer microstructure, and the high fracture toughness is due to the pull-out mechanism of the aragonite “sheet”.

2. SEM observation of the microstructure of Bivalva shell

The molluscan shell used in this study is a Bivalva shell (Unio douglasiae, Figure 1). The SEM samples of the shell were prepared by removing the shell from the mollusc, submerging it in liquid nitrogen for about two minute and then break it down transversely with a small hammer. 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 11000x. SEM observations show that the molluscan shell consists of laminated aragonites and collagen. There are various arrangements, shapes and sizes of laminated aragonites in the shell. Figure 2 shows that the aragonites look like “sheets” packed tightly together and forming planks, and the aragonite planks parallel to the surface of the shell. Figure 3 shows another aragonite microstructure. The aragonites look like “slats” which pack parallel each other, and the aragonite slats consist of thinner aragonite “slats”. Figure 4 shows a long aragonite sheets. These aragonite sheets are with thin and long shape and parallel each other which look like “fiber”. In despite of the different shapes of the aragonites, the aragonites have same characteristics that their smallest composing microstructures are on the nanometer length scale. For example, the smallest aragonite sheets in the shell are from several nanometers to a few ten nanometers in thickness (Figure 2-4), and its nacre layer is made of sheet-like crystals, the sheets is just 0.2-0.6nm in thickness and few micrometer in long.

3. The analysis on nanometer scale of aragonite sheet
The aragonite sheet in molluscan shells (Figure 4) takes on nanometer scale. In this section the reason that the nanometer scales of the aragonite sheets make the shell high fracture strength is analyzed based on the Griffith criterion [6].

Supposing an aragonite sheet with nanometer scale embedded in a collagen matrix, and its direction is parallel to that of loading. The aragonite sheet is with higher Young’s modulus and the collagen matrix with low Young’s modulus. The most of the load is carried by the aragonite sheet. Under this condition, the aragonite sheet must be able to sustain large tensile stress without fracture. Namely, the fracture toughness of the aragonite sheet is closely related to the ultimate strength of the aragonite sheet. It is believed that a perfect (having not flaw) aragonite sheet should possess of
ultimate stress closed to its theoretical strength $\sigma_{th}$. But, in fact, it is ineluctable that there are many defects or flaws in the aragonite sheet. For example, a soft “collagen inclusion” enters into the hard aragonite sheet during the biomineralized process of the aragonite sheet. Because the collagen inclusion have its very low modulus compared with that of its ambient high-modulus aragonite, the tiny “collagen inclusion” can be considered as a flaw in the aragonite sheet. The ultimate strength of the “flawed” aragonite sheet will decrease, and it can be calculated with the Griffith criterion [6]:

$$\sigma^A_h = \alpha E_A \phi, \quad \phi = \frac{\eta}{E_A h},$$  \hspace{1cm} (1)

where the parameter $\alpha$ depends on the crack geometry and is approximately equal to $\sqrt{\pi}$ for the half-cracked aragonite sheet [6]. $E_A$ is the Yong’s modulus of the aragonite sheet, $\phi$ is the volume concentration of the aragonite sheet. $\eta$ is the surface energy and $h$ is the thickness of aragonite sheet. A critical length scale of the thickness of aragonite sheet can be presented [6]:

$$h^* = \alpha^2 \frac{\gamma E_c}{\sigma_{th}^2},$$  \hspace{1cm} (2)

below which the fracture strength of a flawed aragonite sheet is identical to that of a perfect aragonite sheet [6]. Taking a rough estimate $\gamma = 1.5 J/m^2$, $E_A = 150 GPa$, and $\sigma_{th} = E_A / 35$, the thickness of the aragonite sheet can be estimated as $h^* = 40 nm$. This length scale indicates that the nanometer thickness of the aragonite sheet may be the result of fracture strength demand. As the thickness of the sheet drops below this length scale, the strength of an aragonite sheet is ensured and the effect of flaws on the sheet strength can be neglected [6]. This is why the aragonite sheets in molluscan shell take on the nanometer scale.

4. The energy dissipation of pull-out of aragonite sheet from matrix

The aragonite “sheet” observed in the shell is not common in man-made ceramics. The increase of the energy dissipation when pulling a ‘sheets’ out from the matrix is the main mechanism to the increase fracture toughness of molluscan shell [3]. Supposing the aragonite “sheets” embedded in the matrix of molluscan shell were straight and parallel the direction of the traction, the work done by pulling the sheets out from matrix can be estimated with [7]

$$W_p = \frac{V_f \tau_c D^2}{6h},$$  \hspace{1cm} (3)

where $W_p$ is the work dissipated, $V_f$ and $\tau_c$ are the sheet volume fraction and the shear stress of sheet and matrix interface, $D$ is the interval between two lacuna in the sheets [7], which corresponds to the length of pull-out part of the sheet, $h$ is the thickness of sheet. It can be seen from Equation (3) that the larger the sheet volume fraction $V_f$, frictional force between sheet and matrix $\tau_c$ and the interval of two lacuna $D$, the more the work will be dissipated. The larger the thickness $h$ is, the less the fracture work of the ‘sheets’ will be. It can be illustrates why the volume fraction of the aragonite “sheets” is such large (about 95%) and their thickness is such small (unto nanometer scale) in molluscan shell.

5. Conclusions

The SEM observation of Bivalva (Unio douglasiae) shell reveals that the molluscan shell is an organic-inorganic composite laminate. The laminated aragonites embedded in proteinaceous matrix...
and paralleled the surface of the shell. There are various arrangements, shapes and sizes of laminated aragonites in the shell. The SEM observation shows also that the microstructures of the laminated aragonites possess nanometer size. The critical nanometer scale of aragonite sheet in the shell was necessary for holding the high fracture strength of the shell. The energy dissipated during the shell fracture and the aragonite ‘sheets’ pullout mechanism can be used to explain the high fracture toughness of molluscan shell.

Acknowledgement
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).

References