Nanostructure of Nacre and Its Mechanical Effects

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Abstract

A type of nanostructure in the organic matrix interfaces of nacre, which is referred to as mineral bridge in the biomineralization, is directly observed with a transmission electron microscope. It is showed that the existence of mineral bridges in nacre is confirmed. Statistical analysis gives the geometrical characteristics and distribution law of the nanostructure in the organic matrix interfaces. Mechanical experiments and analyses demonstrate that mineral bridges play a key role in mechanical properties of nacre. The nanostructure can not only effectively increase the crack resistance of the organic matrix interfaces, but also automatically form periodic crack resistance to prevent cracks from extending in nacre. This is an indication that the microarchitecture of nacre should be referred to as a "brick-bridge-mortar" arrangement rather than traditional "brick and mortar" one, which gives a conceptual guide to the biomimetic design of synthetic materials.

Keywords: Nanostructure, mineral bridges, nacre, mechanical properties

1. Introduction

The nacre of seashells, which is usually considered as bioceramic, has become an attractive target for the biomimetic design of ceramics in recent years, since its unique microstructure results in light weight materials with high mechanical performance [1-6]. The structure of nacre is traditionally described as a "brick and mortar" (BM) arrangement, where the bricks refer to flat polygonal crystals of aragonite and the mortar is a biological adhesive composed of polysaccharide and protein fibers. However, the study of the structure of nacre has not yet reached maturity. Recent work confirmed that there is many nanopores in the organic matrix layers of nacre, and proposed that there might be some mineral bridges through the pores[9,10]. However, the conclusive evidence of the bridges in the layers of nacre has not given so far. In addition, the relationship between the properties and the structure of nacre have widely studied [3-8,11,12], but the mechanisms based on the structure are not well understood [6,8,12].

In the present study, we give a direct observation of mineral bridges in the organic matrix interfaces of nacre. So the existence of mineral bridges in nacre is confirmed. Statistical analysis gives the characteristics and the distribution of the mineral bridges in the mortars of nacre. Based on the experiments, we find that the mineral bridges not only enhance the crack resistance of the layers of nacre, but also form periodic resistance to prevent cracks from extending in the layers.

2. Structure of the Interfaces

We directly observe the nacre from *H. iris* shells by an H-8100 TEM with a testing table. The microarchitecture of the cross section of nacre reveals a traditional BM (Fig.1a). However, there do exist a lot of nanostructural columns in the organic matrix layers (Fig.1b). The nanostructure, which are traditionally referred to as mineral bridges in the biomineralization, appear to be circular, and stochastically come up in the organic matrix layers. We measured that the diameter of the bridges is 46 ± 8nm, the highness is the thickness of an organic matrix layer, 29 ± 4 nm.

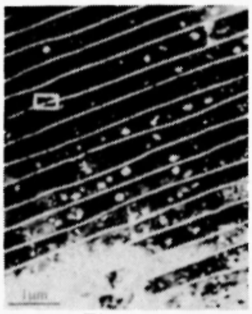

Fig.1a

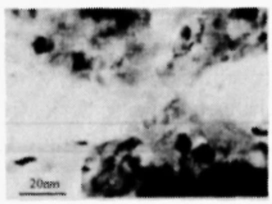

Fig.1b

Fig. 1a TEM image showing the microarchitecture of nacre in the cross section. **b** (the boxed area in **a**) TEM image showing a mineral bridge of nacre.

To study the distribution characteristics of mineral bridges, we randomly choose sixteen platelets from different cross sections of nacre, and determine that the average width approximates L=4μm by measuring the width of the tablets on the cross sections, total bridges of the sixteen tablets count 650 and the average number on each platelet is approximately equal to N_x=40. Furthermore, we divide each of the platelets into n=16 equal units along the direction of organic matrix layer on the cross section, and separately add up the number of mineral bridges (on all tablets) contained by each unit. A histogram of the number of the bridges on the platelets can be given (Fig.2a) and coarsely simulated as $f(x) = N_x \exp[-(x-\mu)^2/2\sigma^2]/\sqrt{2\pi}\sigma$, where μ=8 and σ=2.6 are the average value and standard deviation, respectively; $x(0 \le x \le 16)$ is a local coordinate, the origin of which is one end of the tablet. The local coordinate corresponds to the distance from one end to an arbitrary point of the platelet on the cross section by $l = xL/n$. $f(x)$ expresses the distribution of mineral bridges on the cross section. From $f(x)$, we have $\int_{\mu-\sigma}^{\mu+\sigma} f(x)dx = 0.68N_x$. This is an indication that there exists a central region in each platelet, in which the number of mineral bridges is about 68% that of the whole platelet. The coordinates of the central region is $(\mu-\sigma, \mu+\sigma)$ and the length of the central region, $2\sigma = 5.2$, approximates 1/3 average that of the platelets on the cross section (Fig.2b).

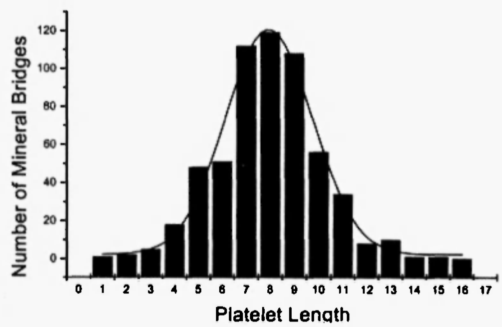

Fig.2a

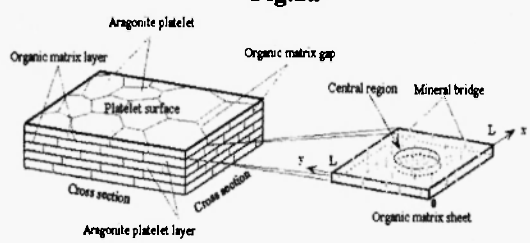

Fig.2b

Fig. 2a Histogram showing the distribution of the number of mineral bridges along the width of platelet on the cross sections. **b** Schematic illustration showing the structure and the mineral bridges in the organic matrix layer of nacre.

3. Crack Resistance in the Interfaces

We choose dry nacre to study the crack resistance of the organic matrix interfaces, and find in the course of the fracture of nacre that: (a) all cracks only extend in the organic matrix interfaces (Fig.3a); (b) the crack path on the cross sections is tortuous; and (c) the crack extension stops after

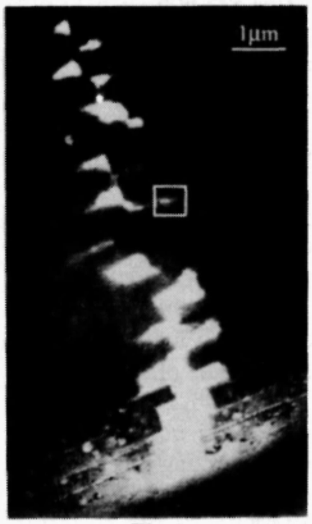

Fig.3a

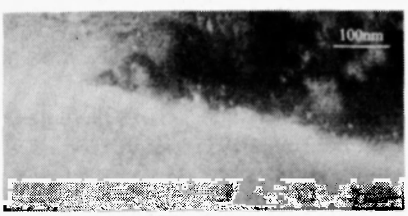

Fig.3b

Fig. 3a TEM image showing a crack extension in the organic matrix layers on the cross section. **b** TEM image showing a crack arrested in the central region.

extending a distance, the length of which is 1.3±0.2μm on cross sections, in every organic matrix layer, i.e. the crack can be arrested in the central region (Fig.3b).

To analyze the effects of the bridges on crack resistance, we take out a sheet of organic matrix from an organic matrix layer between two successive platelets, and assume that the sheet is a square and its area is L^2. Such an organic matrix sheet is approximately treated as a fiber reinforced composite, in which the matrix is organism and the fibers are mineral bridges (Fig.2b). Based on the cross section of nacre, we define a volume fraction of the mineral bridges in the sheet corresponding to an region, (x_1, x_2), as

$$V_b\big|_{x_1}^{x_2} = \pi D^2 N_x \int_{x_1}^{x_2} f(x)dx \Big/ 4L(l_2 - l_1),$$

while the volume fraction of the organic matrix in the region is $V_o\big|_{x_1}^{x_2} = 1 - V_b\big|_{x_1}^{x_2}$, where l_1 and l_2 are two lengths of the sheet corresponding to the local coordinates, x_1 and x_2, respectively; and D=46nm is the average diameter of the bridges. So we give $V_b\big|_0^{16} = 0.17$ to be the average volume fraction of the bridges in the whole sheet and $V_b\big|_{13.4}^{16.6} = 0.35$ in the central region.

When a crack extends in the sheet from x_1 to x_2= x_1+dx, the increment of the fracture work between the organic matrix and platelet is $dW_o = 2\gamma_o(1 - V_b\big|_{x_1}^{x_2})Ldl$; the increment of the work of the mineral bridges fractured is $dW_b = 2\gamma_b V_b\big|_{x_1}^{x_2} Ldl$; and the increment of the fracture work between the bridges and the organic matrix is $dW_{ob} = 2\gamma_o(116V_b\big|_{x_1}^{x_2} \big/ 46)Ldl$. Here γ_o is the average fracture energy between the organic matrix and aragonite; γ_b is the fracture energy of aragonite. Such the crack resistance in the interfaces is $R_c \approx (1 + 1.5V_b\big|_{x_1}^{x_2})R_o$, where $R_o = 2\gamma_o$ stands for the crack resistance of the organic matrix layer without the mineral bridges, γ_b/γ_o is a very small value and neglected. In particular, if the mineral bridges in the sheet are not considered, we obtain R_c=R_o, which is consistent with the results of traditional model of nacre. While in the whole sheet the average crack resistance is R_c=1.26R_o and in the central region the average crack resistance is about R_c=2.04R_o. Obviously, with the crack extends from one end of a platelet into its central region, the crack resistance is rapidly increased to two times. So the cracks are arrested in the central regions of the platelet. In addition, the distribution of the bridges on the cross sections is periodic, the period of which is equal to the average width of the platelets on the cross sections, so the crack resistance is periodic too and its period is the same as one of the bridges.

4. Conclusion

As stated above, the mineral bridges are of importance on the structure and the properties of nacre. The microarchitecture of nacre, thereby, should be referred to as 'brick-bridge-mortar' arrangement instead of traditional 'brick-mortar' one. In addition, it has also been reported that the crystallographic orientations of 3-10 successive platelets on a cross sectional surfaces of nacre can remain the same [13]. So, all these investigations may suggest a bit tangled 'brick-bridge-mortar' structure for nacre.

Acknowledgements

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