ACTA MECHANICA SINICA (English Series), Vol.17, No.3, August 2001 ISSN 0567-7718
The Chinese Society of Theoretical and Applied Mechanics
Chinese Journal of Mechanics Press, Beijing, China
Allerton Press, INC., New York, U.S.A.

MINERAL BRIDGES OF NACRE AND ITS EFFECTS*

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ABSTRACT: Nacre, or mother-of-pearl, is a kind of composites of aragonite platelets sandwiched between organic materials. Its excellent mechanical properties are thought to stem from the microarchitecture that is traditionally described as a "brick and mortar" arrangement. In this paper, a new microstructure, referred to as mineral bridge in the biomineralization, is directly observed in the organic matrix layers (mortar) of nacre. This is an indication that the organic matrix layer of nacre should be treated as a three-dimensional interface and the microarchitecture of nacre ought to be considered as a "brick-bridge-mortar" structure rather than the traditional one. Experiments and analyses show that the mineral bridges not only improve the mechanical properties of the organic matrix layers but also play an important role in the pattern of the crack extension in nacre.

KEY WORDS: mineral bridge, organic matrix interface, nacre, mechanical property

1 INTRODUCTION

Nacre, one of several different kinds of molluscan hard tissue, is a platelet-reinforced composites. In recent years, a great deal of attention has been attracted to investigating the microarchitecture of nacre due to its excellent mechanical properties[1~3]. For example, an abalone nacre has a work of fracture about 3 000 times greater than that of a single crystal of the pure mineral[4,5]. Previous results showed that the strengthening and toughening mechanisms of nacre are determined by its microarchitecture, which, however, has not been identified clearly[4~8]. The traditional model of nacre is considered as a "brick and mortar" (BM) arrangement, where the bricks refer to flat polygonal crystals of aragonite and the mortar, i.e. the organic matrix layer in nacre, is a biological organic adhesive composed of polysaccharide and protein fibers. Recently, some researchers[7,8] proposed that there might be a number of mineral bridges in the mortars, because they found many pores in the organic matrix sheets of nacre. But they did not give a conclusive evidence of the mineral bridges. In addition, to investigate the excellent mechanical performance of nacre, several research groups studied the relationship between the mechanical behaviors and the microarchitecture of nacre[4,5,7,9~12]. However, the possible strengthening and toughening mechanisms based on the microarchitecture are not well understood yet. For instance, Currey[4] and Jackson et al.[5] indicated that the governing factor of the strength and the toughness of nacre is its

Received 31 December 2000, revised 1 June 2001
* The project supported by the Natural Science Foundation of Chinese Academy of Sciences (KJ951-1-201) and the National Natural Science Foundation of China (19891180 and 10072067)

microarchitecture while Smith et al.[12] believed that the key to nacre's fracture resistance resides in the polymer adhesive of the organic matrix.

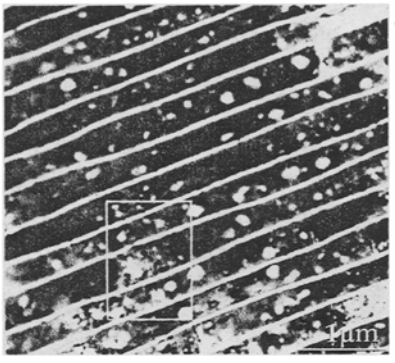
In this paper, a direct observation of mineral bridges in the organic matrix layers of nacre is given. This is an indication that the organic matrix layers of nacre should be considered as three-dimensional structure and the microarchitecture of nacre ought to be described as a "brick-bridge-mortar" (BBM) arrangement rather than the traditional BM one. Our experiments and analyses show that the mineral bridges not only can effectively enhance the stiffness, the strength and the fracture toughness of the organic matrix layers of nacre but also play a significant role in the pattern of the crack extension in nacre. The microstructure of the mortars is a key factor in the mechanical behaviors of nacre, which guides the biomimetic design of the material structure.

2 MICROSTRUCTURE AND MINERAL BRIDGES

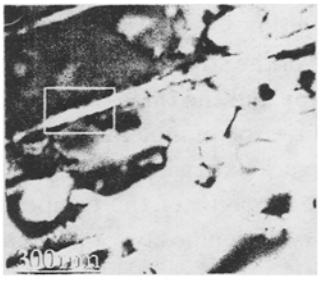
To reveal the microstructure and mechanical properties of nacre, the tests of abalone nacre were performed by an H-800 transmission electron microscope (TEM) with a mechanical testing table at an accelerating voltage of 200 kV. The testing samples are the nacre of an abalone shell from New Zealand, and ceramic composites containing 95vol.% of interlocking aragonite platelets staggered in successive laminae and separated by a 5% organic matrix (Figs.1(a) and (b)). The keratin layer of the shell was mechanically worn off and the residuary part, i.e. the nacre of the shell, was washed with distilled water and air dried at room temperature. Thin films parallel to the cross sectional surface of nacre were cut with a diamond saw, mechanically ground and thin ion-beam milled at an angle of 10° to 50 μm thickness, then perforated under a voltage of 5.5 kV. In the direct observation of the nacre with TEM, the cross sectional surface reveals an aptitude for a BM arrangement (Fig.1(a)). It is estimated that the thickness and width of an aragonite platelet in the cross sectional surface of nacre are 0.37~0.40 μm and 1.8~6.2 μm, respectively. The thickness of an organic matrix interface is 25~32 nm. However, there do exist many mineral bridges in the organic matrix layers (Figs.1(a), (b) and (c)). The mineral bridges appear approximately as circular columns and their positions in the organic matrix sheets are random. The diameter of a mineral bridge is 38~54 nm, and the height of a mineral bridge is equal to the thickness of the organic interface, 25~32 nm. The density of mineral bridges on an aragonite platelet layer is 91~116 μm^{-2}. Therefore, the microstructure of nacre should be referred to as a BBM structure instead of traditional BM one. It has also been reported[14] that the crystallographic orientations of 3~10 successive platelets on a cross section of nacre can remain the same. So, all these observations may suggest a tangled BBM structure.

3 EFFECTS OF MINERAL BRIDGES ON STRENGTH

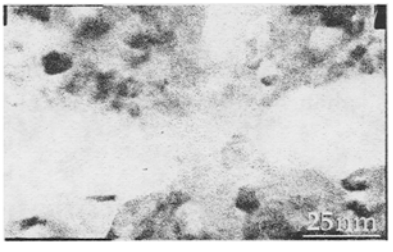
For the analysis of the mechanical properties of nacre, we assume that an interlamellar organic sheet is fetched out from two successive aragonite platelets (Fig.1(d)). Obviously, the mechanical behaviors of the organic matrix sheet are anisotropic due to the microstructure of nacre. It is estimated that a surface area of the organic interface on a platelet is approximately 16 μm^2 while the total cross sectional area of the mineral bridges parallel to the platelet in the sheet is about 2.7 μm^2. Since the area of the latter is about one sixth



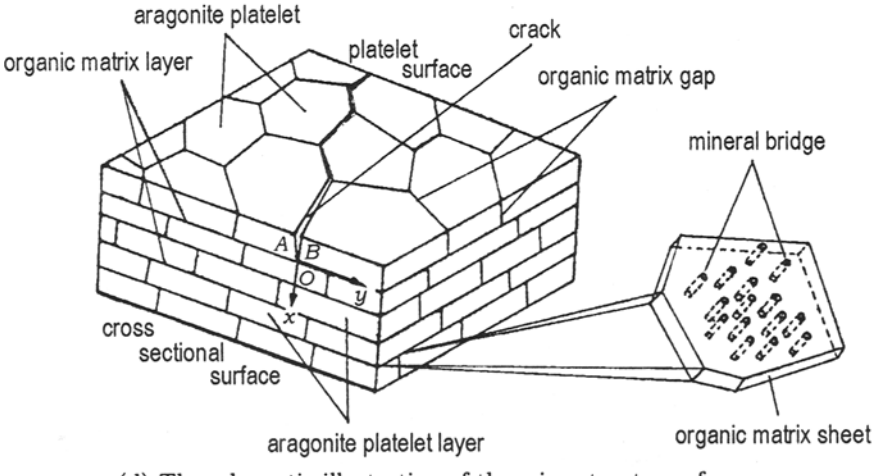
(a) The cross sectional microstructure



(b) The boxed area in (a)



(c) The boxed area in (b)



(d) The schematic illustration of the microstructure of nacre

Fig.1 TEM images and schematic illustration of the microstructure of nacre from abalone shell

that of the former, it is reasonable to treat the organic matrix sheet as a fiber reinforced composites, in which the matrix is organism and the fibers are mineral bridges (Fig.1(d)). We approximately take the Young's moduli of the mineral bridges and the organic matrix as $E_b = 100\,\text{GPa}$ and $E_o = 4\,\text{GPa}$, respectively[5], and the volume fractions of the fiber and the matrix of the composites as $V_b = 1/6$ and $V_o = 5/6$, respectively.

According to the composite theory[15], we obtain Young's modulus as

$$\frac{E_c}{E_o} = V_b \frac{E_b}{E_o} + V_o = 5 \tag{1}$$

where E_c is the Young's modulus of the composites in the direction of the mineral bridges.

If we do not consider the existence of mineral bridges, i.e. $V_o = 1$ and $V_b = 0$, then $E_c = E_o$, Eq.(1) becomes the traditional model of nacre. Equation (1) is an indication that the mineral bridges increase the Young's modulus of organic matrix sheets in the direction of the mineral bridges by five times.

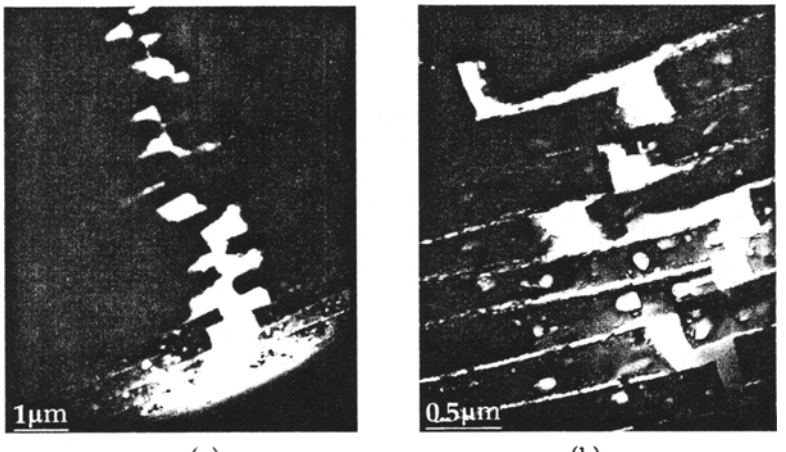
In terms of the strength of the organic matrix layers in the direction of mineral bridges, both the tension and the three-point bending tests of dry nacre show that the organic matrix sheet in the direction of mineral bridges is approximately linear elastic and the strain is very small before crack extension. Since the fraction of the mineral bridges in the sheet is about one sixth, the strength of the composites is controlled by the organic matrix. From the strength theory of composites[15], we have

$$\sigma_c = \sigma_o\left(V_b\frac{E_b}{E_o} + V_o\right) = 5\sigma_o \tag{2}$$

where σ_c and σ_o are the strength of the composites and organic matrix respectively. Equation (2) shows that mineral bridges enhance the strength of organic matrix layers in the direction of mineral bridges by five times.

4 EFFECTS OF MINERAL BRIDGES ON TOUGHNESS

One of the outstanding properties of nacre is its high toughness. To further examine the effect of mineral bridges on the mechanical behaviors of nacre, we performed the tension and three-point bend tests on the nacreous samples that are dry and neither wet nor fresh. Figures 2(a) and (b) show the fracture surface morphology of nacre. We find in the tests that (1) the organic matrix layer in the direction of mineral bridges is approximately linear elastic and the deformation is very small before crack extension; (2) all cracks only extend in the interlamellar organic matrix layers of nacre; (3) the crack path on a cross sectional surface of nacre is tortuous and step wise; (4) crack deflection and aragonite platelet pull-out continually occur in the course of fracture; and (5) the organic matrix bridging, which is one of the main toughening mechanisms of fresh nacre[4,5,7], does not occur in the course of fracture of dry nacre.



(a) (b)

Fig.2 TEM images of the fracture surface of nacre from abalone shell

We firstly analyze the course of the crack extending in nacre. It is assumed that nacre with a crack is in the state of plane stress (or strain) and the stress fields at the crack tip are σ_x, σ_y and τ_{xy}. The crack tip, O, is in the organic matrix layer of nacre since the crack only extends in the layers in the experiments of nacre (Figs.1(d), 2(a) and (b)). Furthermore, we assume that the average strength of the organic matrix layers in the direction of mineral bridges is σ_m and the average shear strength of the layer is τ_m. Obviously, they consist of the contributions of the mineral bridges in the layer. According to the theory of fracture mechanics[16], we have: (1) when $\sigma_x > \sigma_m$, the crack will extend in the layer by the crack mode I; (2) when $\tau_{xy} > \tau_m$, the crack will extend in the layer by the crack mode II; (3) when $\sigma_x < \sigma_m$ and $\tau_{xy} < \tau_m$, the crack does not extend in the layer; and (4) when $\sigma_x = \sigma_m$ and $\tau_{xy} = \tau_m$, the crack is in the critical state of extension. Secondly, we study the direction of the crack extending in the organic matrix layers of nacre. Since the position of mineral bridges in the organic matrix interface is random, the stress fields at the crack tip have stochastic fluctuation which is determined by the density of the mineral bridges in the region near to the crack tip. Our study shows that the stochastic fluctuation of the bridges determines the direction of the crack extending in the organic matrix layer. For example, it is assumed that the average density of mineral bridges in the local region, OA, is greater than that in another local region, OB, as showed in Fig.1(d). So the average strength of the local region, OA, is greater than that of OB, i.e. $\sigma_{mA} > \sigma_{mB}$ in the crack tip region, AOB. Obviously, when the stress field at crack tip satisfies the relation $\sigma_{mA} > \sigma_x > \sigma_{mB}$, the crack extends in the direction of OB by the crack mode I.

Crack deflection is the most commonly observed phenomenon in the course of fracture of nacre, especially when cracking occurs in a direction perpendicular to the aragonite layer. As can be seen in Fig.2, a crack firstly extends along an interlamellar organic matrix layer for a distance which is about three times the thickness of the aragonite platelet. Then the crack extension stops in the interlamellar organic matrix interface and turns 90° to another layer through an organic matrix gap. Such a kind of crack deflection can cause the material to be toughened because of two reasons: (1) the crack extension path is prolonged upon deflection, which implies more energy absorption during its travel; (2) the extension resistance will be raised when the crack diverts to a direction with an unfavorable stress state. Crack diverting always causes the fractured surface to be highly tortuous.

Crack deflection is accompanied by another toughening mechanism, i.e. aragonite platelet pull-out. As showed in Fig.2, cracking occurs mainly along the organic matrix gaps normal to the aragonite layer, while the interfaces along the layers maintain close in contact. Therefore, the mineral bridges and the press forces between the organic phase and the aragonite layer will hinder further development of the crack. Moreover, a platelet pull-out must shear off all mineral bridges connecting with the successive platelets.

As has been indicated above, the excellent fracture toughness of this biomaterial is the result of two toughening mechanisms acting in concert: crack deflection and platelet pull-out. However, these toughening mechanisms are intimately associated with the mineral bridges in the organic matrix layers of nacre. To confirm the conclusion that the mineral bridges play an important role in the fracture toughness of the layers, we still employ the above composite model of the organic matrix layers of nacre. When the effects of mineral bridges in the layer are not considered, we write the fracture toughness of the organic matrix layer as

$$K_{1C}^{o} = \sqrt{2E_o\gamma_o} \tag{3}$$

However, when the existence of mineral bridges is considered in the organic matrix layer, we can give the fracture toughness of the composites as

$$K_{1C}^{c} = \sqrt{2E_c\gamma_c} = \sqrt{2E_c(V_o\gamma_o + V_b\gamma_b + \pi Dt\rho\gamma_o)} \tag{4}$$

where γ_c is the average surface energy of the layer with mineral bridges; γ_o is the average surface energy of the interface between the organic matrix and the aragonite platelet; and γ_b is the fracture surface energy of mineral bridges. In Eq.(4), $\pi Dt\rho\gamma_o$ stands for the surface energy induced by the interactions between the mineral bridges and organic matrix in the composites. By neglecting the contribution of the fracture surface energy of the mineral bridges, $V_b\gamma_b$, and using Eq.(1), and with the average diameter of mineral bridges $D = 46\,\text{nm}$, the average height of mineral bridges $t = 29\,\text{nm}$ and the average density of mineral bridges on one aragonite platelet $\rho = 100\,\mu\text{m}^{-2}$, we obtain

$$K_{1C}^{c} \approx 2.5K_{1C}^{o} \tag{5}$$

This is an indication that the mineral bridges enhance the toughness of organic matrix layers by 2.5 times.

Here we will tackle a problem discussed widely: why the crack stops after extending a distance in an organic matrix layer[4,5]?

On one hand, the experimental data statistics show that the average length of the crack extension on the cross sectional surface of nacre is approximately equal to $1.2\,\mu\text{m}$. It is about one third the average width of an aragonite platelet on the cross sectional surface of nacre, $3.4\,\mu\text{m}$. Only the mineral bridges exist in the organic matrix layer. So it is reasonable to deduce that the mineral bridges prevent the crack from extending in the organic matrix layers of nacre.

On the other hand, according to the theory of fracture mechanics[16], we rewrite the fracture toughness of materials as

$$K_{1C} = \sigma\sqrt{\pi a} \tag{6}$$

where σ is the strength of material and a is the half length of crack. Substituting Eqs.(2),(3) and (5) to (6), yields

$$\frac{a_c}{a_o} = 2.5^2\left(\frac{\sigma_o}{\sigma_c}\right)^2 = \frac{1}{4} \tag{7}$$

where a_c and a_o are the half length of crack in the organic matrix layer with and without mineral bridges, respectively. Equation (7) shows that the length of the crack extension in an organic matrix layer without the mineral bridges should be four times that of a real crack measured from the experiments of nacre. This is an indication that the mineral bridges effectively hinder the crack extending in the organic matrix layers.

5 CONCLUSIONS

Based on the direct observation of the cross sectional surfaces of nacre by TEM, we confirm the existence of mineral bridges in the organic matrix layer of nacre. All mechanical experiments and analyses of nacre indicate that mineral bridges effectively increase the stiffness, strength and toughness of the organic matrix layers, and demonstrate that the

effects of the mineral bridges on the organic matrix layers are of importance. It can be seen that the excellent toughness of this biomaterial is the result of two toughening mechanisms acting in concert: crack deflection and platelet pull-out. These toughening mechanisms are intimately associated with the mineral bridges in organic matrix layers, and are also direct results of the unique microstructure of nacre. It is the existence of mineral bridges in the weak layers of nacre such that synthetic biomimetic materials with BM structure do not have a toughness comparable to nacre.

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