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Observations of damage morphologies in nacre during deformation and fracture

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The deformation, fracture and toughening mechanisms of nacre from a kind of fresh-water bivalve mollusc (*Cristaria plicata*) were studied by SEM, TEM and microindentation tests. Experimental results revealed a strong anisotropy of the damage behaviour reflecting the microstructural character of nacre. The fractured surface parallel to the cross-sectional surface of nacre was much more tortuous than that parallel to the platelet surface. The crack line on the cross-sectional surface was step-like, while that on the platelet surface was polygonal. Sliding of aragonite layer combined with the plastic deformation of organic matrix is the main plastic deformation mechanism of nacre. Three main toughening mechanisms have been found acting in concert: crack deflection, fibre pull-out and organic matrix bridging.

1. Introduction

Mother-of-pearl, or nacre, is one of the biological hard tissues which have received much attention in recent years [1–9]. It is a ceramic composite containing highly organized and polygonal-shaped aragonite platelet layers with a thickness of 0.25–0.99 μm, separated by a thin layer of protein-polysaccharide matrix (30–50 nm thick) [3–10]. Such an organization is similar to a "brick and mortar" structure. Because of its particular microarchitecture, the strength and fracture toughness of nacre are many orders of magnitude higher than those of monolithic aragonite, and are comparable to or better than those of synthetic ceramic materials [2, 3, 10–12].

In order to reveal the nature of its excellent performance, and to draw some guideline for the design of better composites, several groups have studied the relationship between the mechanical properties and the microstructure of nacre [10, 11, 13–15]. Previous results showed that the mechanical properties of nacre are anisotropic [10, 11], and nacre undergoes a marked plastic deformation before fracture, with a maximum strain of 0.018 [10]. However, the deformation mechanism, the damage and crack propagation behaviour and the possible toughening mechanisms are not well understood. Having decided that tension and bending, which are commonly used in the study of nacre, do not easily reveal the deformation and fracture process because of the low fracture strain of nacre, the microindentation test was selected in this work in an attempt to study the deformation and fracture behaviour of this material.

2. Experimental procedure

All tests were performed on nacre from the shell of a bivalve mollusc, *Cristaria plicata* (Leach), cultivated in Zhenjiang, in the southeast of China. Fig. 1 shows the microstructure of this kind of nacre; its composition and structural parameters are listed in Table I (for details see [16]). Specimens of nacre, 6.0 mm wide, 8.0 mm long and 0.8 mm thick, were washed with distilled water and air dried at room temperature. Microindentation experiments on both the platelet surface, which is parallel to the shell interior surface, and the cross-sectional surface, were performed on a HX-200 microindentor employing Vickers geometry with a load of 0.2 kg. The indentation zone and fracture surface morphologies were analysed using a Hitachi S-550 scanning electron microscope (SEM) at 25 kV. Thin foils parallel to the cross-sectional surface were mechanically ground and ion-beam milled, and then were observed in a H-800 transmission electron microscope (TEM) at an accelerating voltage of 200 kV.

3. Results and discussion

3.1. Fracture and microindentation morphology

The morphologies of the fractured surfaces are shown in Fig. 2. When nacre was broken up parallel to the platelet surface, the fractured surface is relatively smooth, as shown in Fig. 2a, where fracture involves only a few layers of aragonite platelets, while the fractured surface parallel to the cross-sectional surface is quite rough, with the crack always deflecting in adjacent platelets (Fig. 2b). Therefore, the crack propagation path in the latter case is evidently much longer than that in the former case, which in turn absorbs more energy during the process of fracture. Obviously, the above anisotropy in fracture behaviour is closely related to the highly ordered microarchitecture of nacre and is the main reason for the anisotropy in mechanical properties [10, 11].

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Microindentation tests indicate that both the microhardness and the indentation morphology are anisotropic and strongly reflect the ordered microarchitecture of nacre. The mean microhardness on the polished platelet surface is 198 MPa, while that on the cross-sectional surface is 220 MPa. Fig. 3a and b give two typical morphologies of the indentations, from which at least two main differences can be seen between the indentation morphology on the platelet surface and that on the cross-sectional surface: first, the four edges of the indentation on the platelet surface are curved and obscure (Fig. 3a), while those on the cross-sectional surface are relatively straight and clear (Fig. 3b); second, on the platelet surface, cracks can be seen on all of the four edges, and the shape of these cracks is irregular (Fig. 3c), while on the cross-sectional surface, cracks only exist on those edges normal to the aragonite layer, and the cracks in this case are more regular, often step-like (Fig. 3d). No cracks are found on those edges parallel to the layer.

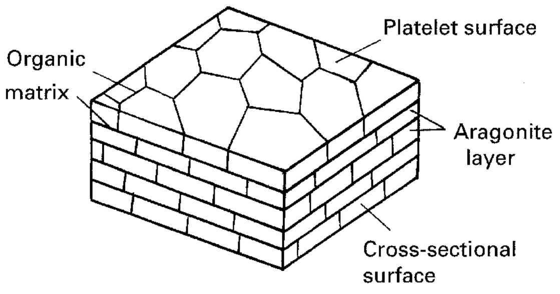

Figure 1 Schematic illustration showing the microarchitecture of nacre and the testing planes of microindentation.

TABLE I Compositions and structure of the tested nacre

Ceramic phase	Organic matrix
$CaCO_3$ (aragonite), ~ 95 vol %	Protein and polysaccharide [7], ~ 5 vol %
Polygonal platelet, 0.5 μm thick, 2.8 μm diameter, organized in layers	Thin organic layer, ~ 30 nm thick, between aragonite layers and platelets

Anisotropy in the indentation morphology has also been observed in natural ivory [17], where it was found to be the direct result of the anisotropic character in the microstructure of this biological composite. When Fig. 3 is considered with the microstructural character of nacre, the same conclusion can also be made. As has been found, the microarchitecture of nacre is anisotropic, and the aragonite platelet is polygonal and interlocks perfectly with its neighbour to form layers which are stacked on top of each other in a staggered formation; between these platelets is the relatively weak organic matrix (as illustrated in Fig. 1) [3–10]. Therefore, when the platelet surface is pressed by an indentor, a crack will initiate and propagate along the weak organic matrix between the polygonal platelets. Evidently, this type of crack line is polygonal, reflecting the characteristic shape of the aragonite platelet, as shown in Fig. 3c; this in turn makes the indentation edges curved and obscure (Fig. 3a). When cracks are produced on the cross-sectional surface, they will propagate either along the parallel thin organic layers lying between aragonite layers, or cut through the organic phase within the aragonite layer (Fig. 3d). This type of step-like crack can be seen more clearly in Fig. 4, where Fig. 4a is

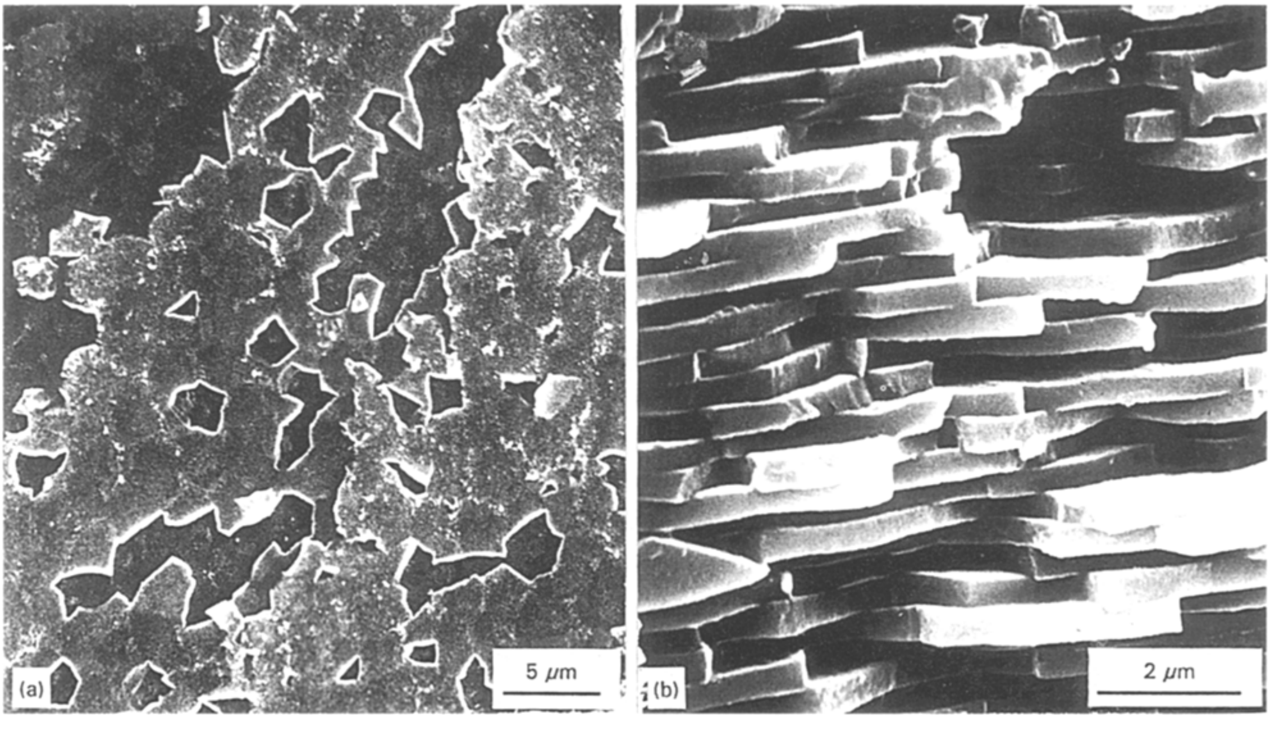

Figure 2 Scanning electron micrographs of the fractured surface of nacre, (a) fractured parallel to the platelet surface, (b) fractured parallel to the cross-sectional surface.

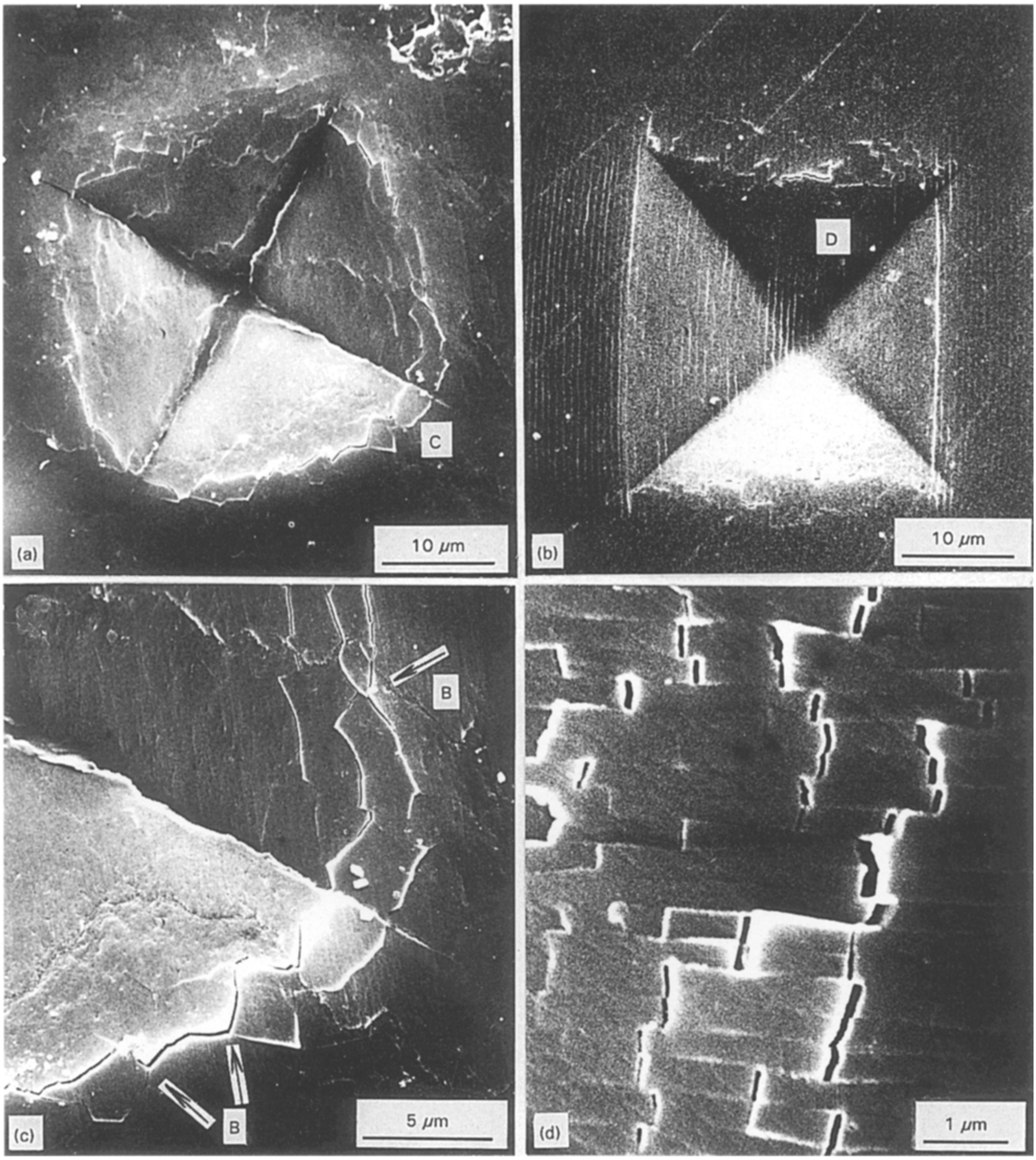

Figure 3 Morphologies of the microindentation zone on different surfaces of nacre: (a) platelet surface; (b) cross-sectional surface; (c) magnified figure of area C in (a); (d) magnified figure of area D in (b).

observed near the fractured surface shown in Fig. 2b, and the crack in the transmission electron micrograph of Fig. 4b is caused by the thermal stress induced by ion milling during sample preparation. When the indentation edges are parallel to the aragonite layer, it will be difficult for cracking to occur due to the plastic deformation involving sliding of aragonite layers, which will be discussed below. As a result, the indentation edges are straight and easy to see.

3.2. Deformation behaviour

In order to investigate the plastic deformation behaviour of nacre, microindentation tests on the cross-sectional surface were carried out at one edge of the specimen; then the indentations were observed from another cross-sectional surface perpendicular to the indentation plane. The result is shown in Fig. 5, from which it can be seen that there is a remarkable displacement of the aragonite layer relative to its neighbour in the loading direction, and the organic matrix between the aragonite layers shows considerable plastic deformation, but retains its adhesion to both of them (see the organic ligaments indicated by arrows in Fig. 5b). These results clearly indicate that the deformation of nacre has taken place via the sliding of the aragonite layer which is realized by the plastic deformation of the organicmatrix between them. In the

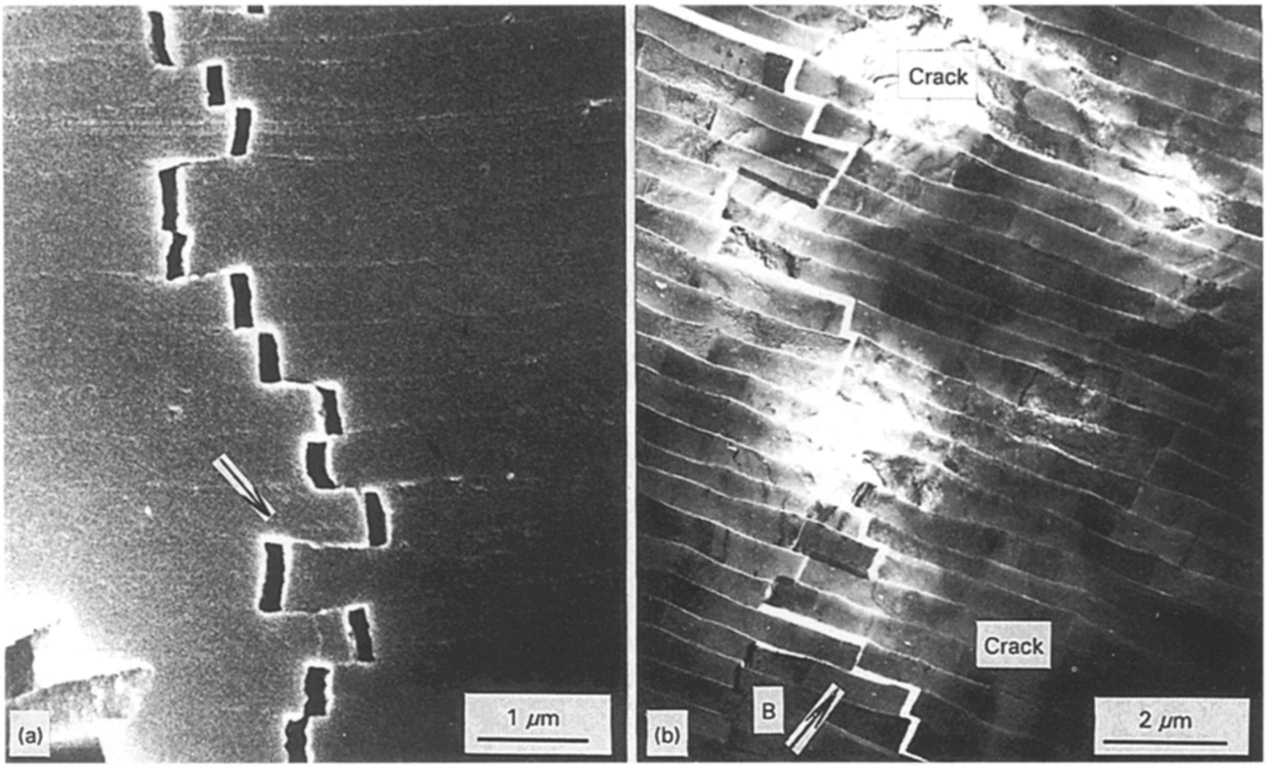

Figure 4 Crack morphologies of nacre on the cross-sectional surface; (a) scanning electron micrograph of the area near the fractured surface of Fig. 2b; (b) transmission electron micrograph.

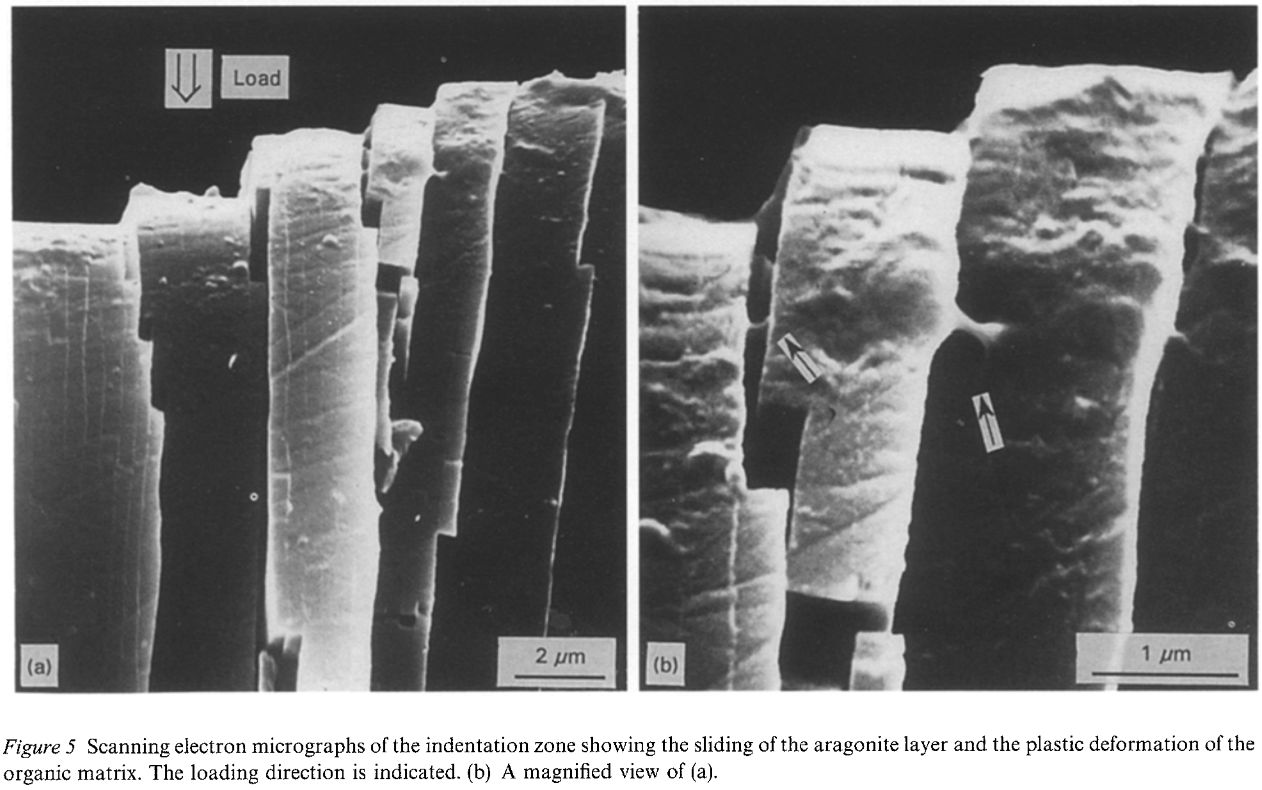

Figure 5 Scanning electron micrographs of the indentation zone showing the sliding of the aragonite layer and the plastic deformation of the organic matrix. The loading direction is indicated. (b) A magnified view of (a).

tension test, Currey [10] found that nacre can endure marked plastic straining before fracture. He also suggested that this is unlikely to be due to the plastic deformation of the aragonite platelet because of the relatively low stresses occurring in nacre, but has something to do with the plastic deformation of the matrix. From our observations discussed above, it can be seen that sliding of the aragonite layer is a main deformation mechanism, and the organic matrix plays an important role by accommodating the sliding deformation between the layers. The sliding of the aragonite layer is the main reason for the cracking anisotropy observed in Fig. 3b. When the indentation edges are parallel to the aragonite layer, nacre can endure plastic deformation by sliding of the aragonite layer, and hence cracking does not occur easily. When the indentation edges are perpendicular to the layer, such a sliding process is greatly restricted, and thus causes cracks to appear.

3.3. Toughening mechanisms

One of the most outstanding features of nacre is its high toughness. Therefore, the toughening mechanisms and their guide to materials synthesis are of common interest. The SEM and TEM results of the crack propagation experiments on nacre show that a crack propagates along the organic phase in most cases (see Figs 3c, d and 4), which coincides with other results [9–11, 14]. So the organic matrix plays an important role in the toughening of this biological composite. From the crack morphologies, it is found that crack deflection, fibre pull-out and organic matrix bridging are the three main toughening mechanisms acting on nacre, although other mechanisms also exist (e.g. crack branching at B in Figs 3c and 4b).

Crack deflection is the most commonly observed phenomenon in nacre, especially when cracking occurs in a direction perpendicular to the aragonite layer. As can be seen in Fig. 4, a crack first propagates along an interlayer boundary for a distance, and traverses the aragonite layer, then turns to another interlayer boundary. Such a kind of crack deflection can cause the material to be toughened because of two reasons: first, the crack propagation path is prolonged upon deflecting, which implies more energy absorption during its travel; second, the propagation resistance will be raised when the crack deflects to a direction with an unfavourable stress state. Crack deflection always causes the fractured surface to be highly tortuous, as shown in Fig. 2b.

Crack deflection is often accompanied by another toughening mechanism, fibre pull-out. As indicated by arrows in Fig. 4a, cracking occurs mainly along the interfaces normal to the aragonite layer, while the interfaces along the layers maintain close contact. Therefore, the binding forces between the organic phase and the aragonite layer will hinder further development of the crack. This is the fibre pull-out (here the “fibre” is the aragonite platelet) toughening mechanism discussed by Sarikaya *et al.* [14].

Fibre pull-out and crack deflection are two common toughening mechanisms found in synthetic fibre-reinforced ceramics [18, 19], and it has been recognized that a weak fibre–ceramic matrix interface is very important for the two mechanisms to act [20]. Therefore, many attempts have been made to obtain an appropriate interfacial strength so that a crack can be easily deflected at the interface [20, 21]. From the viewpoint of interfacial strength design, nacre is an ideal composite, which is composed of inorganic ceramic phase (aragonite) and the organic matrix organized in an ordered way. The organic matrix between aragonite layers is weak relative to its ceramic component, and it is easier for a crack to propagate along the organic matrix than to penetrate the hard ceramic phase. As a result, crack deflection and fibre pull-out occur easily.

One toughening mechanism in nacre which does not exist in synthetic ceramic composites is that of organic matrix bridging. As shown in Fig. 5b, the organic matrix adheres to the adjacent aragonite layer during deformation and cracking of nacre. Such adhesion is a common phenomenon in nacre [9, 11, 14], which shows that there is a strong interface between the organic phase and the aragonite platelets, and therefore, its contribution to the toughness is not negligible. It increases the slip resistance between the adjacent aragonite layers, and enhances the toughening effect of fibre pull-out. On the other hand, it acts as a bridge linking the separating aragonite layer, and lowering the stress intensity factor at the crack tip, thus increasing the crack-propagation resistance and toughening the material. Here, we call this toughening mechanism organic matrix bridging.

From the results discussed above, it can be seen that the excellent toughness of this biomaterial is the result of several toughening mechanisms acting in concert: crack deflection, fibre pull-out and organic matrix bridging, and these toughening mechanisms are, in turn, direct results of the unique microstructure of nacre.

4. Conclusion

The fracture and microindentation zone morphologies, as well as the cracking behaviour of nacre, are anisotropic, and strongly reflect its microstructural character. The fracture surface parallel to the cross-sectional surface of nacre is much more tortuous than that parallel to the platelet surface, and the crack line on the cross-sectional surface is step-like, while that on the platelet surface is polygonal. Sliding of the aragonite layer combined with the plastic deformation of the organic matrix is the main plastic deformation mechanism of nacre. There are three main toughening mechanisms acting in concert: crack deflection, fibre pull-out and organic matrix bridging.

Acknowledgement

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