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OF SEVERAL MOLLUSK SHELLS

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THE MICROINDENTATION BEHAVIOR OF SEVERAL MOLLUSK SHELLS

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ABSTRACT

An investigation of the relationship between structure and mechanical behavior is reported for mollusk shells employing foliated, nacreous, and crossed-lamellar structures by microindentation in the Knoop and Vickers geometries. Indentation damage zones develop crack systems that reflect the micro-architecture. For the crossed-lamellar structure, the system of cracks about the indentation normally developed in a brittle material is suppressed. Previous reports that shells are harder than the corresponding minerals, calcite and aragonite, are confirmed, but it is found that this effect can be strongly dependent on orientation. This anomalous hardness is not an artifact of the indentation test technique, since scratch tests confirm the relative hardness of shell over the mineral. It is suggested that microstructural organization is of central importance in producing this hardness, as opposed to intrinsic properties of the mineral or matrix phases.

INTRODUCTION

Biological hard tissues are load-bearing structural materials, composed of a mineral component and an organic component. They appear in diverse situations where, among other properties, strength, abrasion resistance, impact resistance, density, elastic moduli, and fatigue properties are of importance. Mollusk shells are interesting examples of hard tissues because their properties can be conveniently compared to structural ceramics and ceramic composites, as these shells typically contain a smaller fraction of organic material (<5 wt.%) than many other hard tissues, e.g., mammalian bone (often >40 wt.%). Moreover, a variety of microstructural types [1] (or micro-architectures) and two different polymorphs of CaCO_3 are frequently employed in molluscan shell. These microstructural variations present a unique opportunity to pursue understanding of the relationship between microstructure and properties in this class of materials.

Mollusk shells exhibit remarkably high flexural and compressive strengths [2-5], often in excess of 300 MPa. They also are very resistant to fracture. For example, fracture toughness between 5 and 11 $\text{MPa}\cdot\text{m}^{1/2}$ have been reported for nacreous shell [4]. Crossed-lamellar shell can undergo non-catastrophic failure in bending [3,5], suggesting a level of toughness that is completely unexpected from a material that contains at most 0.5 wt.% of organic material [2,6].

One of the most interesting aspects of the mechanical properties of mollusk shells is the report [2] that the hardness of all shell structures exceeds that of the minerals, calcite and aragonite. This anomalous hardness has never been adequately explained, although it was originally suggested that the effect may result from enhanced elastic accommodation of the applied stress, associated with the intrinsic elastic properties of the organic matrix, i.e., its low elastic modulus.

The inhomogeneous, highly ordered and anisotropic nature of these composites complicates the interpretation of bulk mechanical tests. Microindentation experiments, on the other hand, apply a reproducible load with known geometry to an isolated portion of the microstructure. This localization and the anisotropy of the applied stress can be used to advantage in investigating the relationship between microstructure and properties.

This paper reports microindentation studies of three mollusk shells. The questions of interest are: (1) What can be said quantitatively about the properties? (2) What are the phenomena and underlying mechanisms observed in the vicinity of the indentation, i.e., in the damage zone? and (3) Are shells actually harder than native calcite and aragonite, and if so, why?

EXPERIMENTAL

Dry shells from the species *Strombus gigas* or "pink conch", *Ligumia nasuta* (a small fresh-water clam) and *Pecten caurinus* (a large scallop), were used in this study. Indentation experiments were performed on a Zwick microindenter employing Vickers and Knoop geometries at room temperature over a range of loads from 0.1 Kg to 10 Kg. Indentations were separated by at least 5 indentation diameters from one another and from

the specimen edge, and the specimen thicknesses were well in excess of 5 indentation diameters. Indentation and damage zone morphology were determined by optical and scanning electron microscopy.

RESULTS AND DISCUSSION

Indentation tests were performed on polished surfaces approximately parallel to the shell interior surfaces, i.e., the surfaces that would be adjacent to the mollusk *in vivo*. This orientation was chosen in order to provide a consistent orientation with respect to the macroscopic shell architecture.

The Knoop geometry was used to measure the load dependence and orientation dependence of the hardness. The Vickers geometry was employed to investigate the mechanical behavior in the damage zone. A complex system of cracks often develops about Vickers indentations in brittle materials [7], e.g., the so-called median, lateral, and radial cracks. Some of these features appear in the damage zones for the materials tested here. However, the details of these features are strongly affected by the anisotropy of the microstructure, and in some conditions these characteristic features of brittle behavior are altogether suppressed.

Figure 1. SEM micrograph of an indentation on the shell interior surface of *Strombus gigas*, which employs the crossed-lamellar structure.

Microstructure and Damage Zone Phenomena

Strombus gigas:

This conch shell is composed of three layers of crossed-lamellar shell (for a complete discussion of its microstructure, see Ref. [8] (this Proceedings)). This microstructure is constructed from lath-like grains of aragonite (typically $1\ \mu\text{m} \times 200\ \text{nm} \times 40\ \text{nm}$), which are assembled in an ordered fashion to form larger laths. These large laths are called second-order lamellae and are typically $20\ \mu\text{m} \times 1\ \mu\text{m}$ in cross-section and can extend for hundreds of μm in length. Second-order lamellae are stacked to form plates, called first-order lamellae, with neighboring plates alternating between two distinct orientations.

Figure (1) is an SEM micrograph of a typical Vickers indentation upon the shell interior surface. The indentation is large enough to straddle several first-order lamellae. The damage zone is elongated parallel to first-order lamellae and contains coarse lamellar features, apparently arising from these lamellae. These features suggest that extensive plastic deformation is occurring in a larger region than would be expected for a typical brittle material, and the mechanism of deformation appears to be sliding of lamellae. This might occur by plastic deformation of the organic matrix phase during sliding or by delamination at the boundaries between lamellae prior to sliding.

Pecten caurinus:

Figure 2. SEM micrograph of the fracture surface of the shell of *Pecten caurinus*. The organization of the laths of the foliated structure into a sheet or lamella is apparent.

This scallop shell is calcitic, and employs the so-called *foliated* structure. This structure is also constructed from laths, arranged to form sheets that are nearly parallel to the shell interior surface. The laths in foliated shells are typically 2-4 μm wide and less than 500 nm thick, extending for hundreds of microns in length. They are arranged into many highly ordered domains, which are assembled into sheets about 40 μm thick. These features are shown in Figure (2), an SEM micrograph of the fracture surface.

Figure (3) shows an optical micrograph of an indentation in this material. Although some radial cracking is present, there is extensive lateral cracking approximately parallel to the test surface, which gives rise to the interference fringes at the periphery of the damage zone. It is likely that these cracks run parallel to the boundaries between sheets in the foliated structure.

Ligumia nasuta:

The shell of this small fresh water clam contains an inner *nacreous* layer and an outer *prismatic* layer. Figure (4) is an SEM micrograph of a fracture surface showing the tabular grains of aragonite that make up the nacreous structure. The shell interior surface is parallel to the plane of these plate-like grains. Figure (5) shows an optical micrograph of a Vickers indentation, loaded on a polished surface nearly parallel to the shell interior surface. The lobes extending from the edges of the indentation are due to lateral cracking beneath the surface. These cracks most likely follow sheet boundaries in the nacreous structure, as in the foliated structure.

Microhardness

Table I is a summary of the Knoop indentation data for the three shells and single crystal calcite. Most of the data display a load dependence; the hardness decreases with increasing applied load. A load dependence of this kind is not unusual in microindentation for metals, ceramics, and other materials. It is generally thought that this load dependence arises from an overestimate of the hardness at low loads, and it has been suggested [9] that the effect results from localization of plastic deformation. In materials that deform in this way, additional plastic deformation always requires the formation of a new "band" of localized deformation. If the indentation size is comparable to the scale of localization, difficulties in nucleating a new band of localized deformation could produce a large error in the measured hardness.

Figure 3. Optical micrograph of Vickers indentation on the interior surface of the *Pecten* shell. Interference fringes appear at the periphery of a lateral crack that is parallel to the test surface.

Figure 4. SEM micrograph of the fracture surface of the nacreous structure in the shell of *Ligumia nasuta*. The test surface for indentations is parallel to the sheets of tabular grains of aragonite.

Table I. Knoop Microhardness Data (in GPa)				
	0.2 Kg	0.5 Kg	1.0 Kg	2.0 Kg
Calcite	1.3	1.0	0.9	-
Scallop	2.0	1.9	1.5	1.5
Clam	-	1.9	2.0	1.8
Conch(N)	1.9	1.8	1.7	1.6
Conch(P)	3.2	2.8	2.6	2.3

For small loads, e.g., 0.2 Kg, the data for single crystal calcite agree with the published hardness of mineral calcite [2]. The calcitic shell of the scallop (*Pecten*) is harder than the native calcite at every applied load investigated. For applied loads above 1 Kg, the measured hardness approaches the published value for calcite, but the measured hardness of the mineral falls off well below this value.

The foliated structure (scallop) and the nacreous structure (clam) show very little dependence of hardness on orientation in the plane of the shell interior surface. This is consistent with the fact that these shell architectures orient sheets of material approximately parallel to this surface. On the other hand, the hardness of the crossed-lamellar structure in *Strombus* exhibits a marked orientation dependence. The "soft" orientation corresponds to placing the long axis of the Knoop indenter *normal* (N) to the first-order lamellae. The hard orientation is *parallel* (P) to these lamellar features. This probably results from the fact that plastic deformation involves sliding of lamellae. When the Knoop indenter is in the normal (soft) orientation plastic deformation can occur in several first-order lamellae, but in the parallel (hard) orientation the deformation is limited to one or two first-order lamellae. The hardness in the soft orientation is comparable for large loads to that of mineral aragonite [2], about 1.8 GPa, while that in the hard orientation is consistently around 50% greater than in the soft orientation over the entire range of loads.

The calcitic shell clearly has a higher value of Knoop hardness than the mineral calcite. Two possible explanations exist. Either it is more difficult to induce permanent plastic deformation in the shell due to the unique shell microstructure (micro-architecture), or the higher measured hardness is an artifact of the microindentation technique. In the latter case, the effect should be absent from a hardness test that does not use the indentation geometry, such as a scratch test or other tribological techniques. In fact, the calcitic shell can easily produce deep scratches visible to the naked eye on polished surfaces of a single crystal of calcite, but polished surfaces of the shell are not scratched by the mineral. An optical micrograph of such a scratch on a calcite surface is shown in Figure (6). This experiment confirms that the anomalous hardness is not simply an artifact of the test technique.

In principle, the increased hardness of shell might result from intrinsic hardening of the mineral, intrinsic matrix effects, or composite effects associated with the microstructural design. In the aragonitic crossed-lamellar shell (*Strombus gigas*), the orientation dependence of the hardness indicates that microstructural organization can play an important role in enhancing the hardness. The fact that both aragonitic and calcitic shells have higher hardness than the respective minerals emphasizes this point, as the mechanical behavior of aragonite is quite different from that of calcite [10]. It therefore seems likely that microstructural design is responsible for at least part of the hardness increase. Intrinsic hardening of the mineral and intrinsic matrix effects appear to be less important. For example, the soft orientation of the crossed-lamellar structure has hardness comparable to mineral aragonite, even though the aragonite grains contain a high density of defects (twin boundaries) in the *Strombus* shell [8].

It is not possible to propose detailed mechanisms for the influence of microstructural order on the hardness, based on the present data. Since the microstructures are highly ordered, the usual arguments for dislocation pile-ups at grain boundaries owing to incompatibility of slip systems in neighboring grains are probably not acceptable explanations. Hence, the hardness increase is probably not a straightforward example of

Figure 5. An optical micrograph showing a Vickers indentation on the interior surface of the nacreous layer of *Ligumia*. Lobes around the indentation are caused by lateral cracking beneath the test surface.

Figure 6. An optical micrograph of a scratch produced on a polished surface of mineral calcite by abrasion against the edge of the *Pecten* shell, which is calcitic. The conjugate scratch test of the surface of the shell with a sharp edge of the calcite crystal produced no scratch.

the Hall-Petch [11,12] grain size effect. It is possible, however, that the anomalous hardness comes about because of difficulty in introducing dislocations into the neighboring grains for other reasons. The organic matrix is expected to behave in a visco-elastic manner, and may actually serve to blunt stress concentrations at the grain boundaries that would otherwise propagate slip from one grain to the next. It is observed that in the *Strombus* shell, considerable deformation occurs at the lamellar boundaries around a Vickers indentation (Fig. 1) and that this mode of deformation is accentuated along the indenter diagonal that lies along the "hard" orientation of the Knoop tests. This is interesting because it may indicate a correlation of the hardness increase with deformation of the organic matrix phase at the boundaries. These observations emphasize the need for further work to determine the mechanisms of deformation that occur in these materials, both in indentation and in other test geometries.

CONCLUSIONS

Two of the three shell structures investigated here, the foliated and the crossed-lamellar structures, are harder than the corresponding monolithic minerals when tested on the shell interior surface. This anomalous hardness cannot be explained without considering the microstructural order, as evidenced by the orientation dependence of the Knoop hardness of the crossed-lamellar structure. Examples of radial and lateral crack systems are found in the indentation damage zones, but their occurrence and morphology are strongly influenced by microstructural features. Lateral cracking occurs in the nacreous and foliated structures when the load axis is normal to the "sheets" of mineral. In the crossed-lamellar shell of *Strombus*, plastic deformation by sliding of lamellae along the lamellar boundaries suppresses the development of these crack systems for all loads tested, up to 10 Kg.

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