LOCAL ORIENTATION ANALYSIS OF ABALONE NACRE BY MICRO-BEAM LAUE DIFFRACTION

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Summary. Micro-beam Laue diffraction experiment was carried out on beamline BM32 at ESRF (Grenoble, France). The nacreous layer of green abalone shell was studied. Quantitative analysis of the results allows the characterization of the local crystal misorientation within the nacreous layer. LaueTools software [1] was used to determine the c-axis orientation distribution of aragonite tablets in the nacreous layer, and more specifically, the degree of misorientation with respect to the pure [001] direction. This reflects how the adjustment of crystal orientation occurs during nacre growth, and the resulting micro-structure in turn is likely to determine the strengthening and toughening mechanisms in nacre. This level of understanding is crucial for implementing the biomimetic agenda.

1 INTRODUCTION

Nacre, or mother-of-pearl, is a typical biomineralisation product that has provided the motivation for numerous studies into the details of its micro- and nano-structure because of its remarkable mechanical properties [2]. However, the formation (growth) mechanisms is not completely understood. The nacreous layer is composed of about 95% inorganic tablet-shaped single crystals of thin aragonite (a mineral form of CaCO$_3$) by weight with a thickness of 0.25-0.4µm and edge lengths of 5-10µm (aspect ratio <0.1) [3]. All these flat tablets are oriented with the c-axis aligned almost normal to their interface i.e. the tablets are arranged like brick-mortar architecture [4]. Such characteristic microstructure gives nacre a higher toughness compared to the geological aragonite CaCO$_3$ [5].

Recent studies have demonstrated that the c-axis of different nacre tablets are not all perfectly parallel to each other between subsequent layers (by traversing a cross-section) [2]. The orientation inhomogeneity may demonstrate that nature makes ingenious use of small
crystal misorientations in order to optimize the mechanical performance in terms of the strength and toughness of these composite structures. These intricate interrelationships have long fascinated scientists, but have not yet been well explained [6]. Therefore, understanding the micro-/nano-scopic origin of the macroscopic properties achieved by nature’s ingenious designs is of great importance.

Micro-beam Laue diffraction technique is regarded as a particularly useful tool to probe local (grain level) lattice orientation. The principle is akin to the classical Laue diffraction in which a single crystal sample is illuminated with a polychromatic beam. The strong demand for structural characterization of objects with ever decreasing sizes has driven forward the development of micro-beam Laue diffraction method, and made BM32 at ESRF an attractive beamline for research on hard tissue microstructure of biomaterials.

In this paper, presence of small tablet misorientation on nacreous surface of green abalone seashell was investigated by micro-beam Laue diffraction experiment. We hope the investigation of misorientation may help understand the remarkable toughening effect achieved by the characteristic “roman brick wall” micro-structure and ultimately allow better biomimetic materials to be made.

2 RESULTS AND CONCLUSIONS

The interpretation of the Laue patterns from the nacreous layer shows that the overall alignment of the c-axis of aragonite tablet is such that the [001] direction is almost coincident with the surface normal, as expected. However, not only the shell itself is curved, but even
within a small region of nacreous surface small misorientation exists compared to pure [001]. This is illustrated in Fig. 1 (a) and (b), which may reflect how the adjustment of crystal orientation occurs. The direction of pure [001] direction is along the z-axis in Fig. 1(a), and each 3D vector represents the direction of c-axis in nacreous layer for each scanned point. Four distinct arrow colours were ascribed based on the tablets (grains) distribution in Fig 2 (a), and used to distinguish between adjacent regions. The length of the projection arrow (Fig. 1(b)) indicates the vector deviation from z-axis, i.e. if it stays along z-axis perfectly, the projection should be a point. The longer the line is, the bigger the misorientation will be for each position. Meanwhile, the direction of the short line in x-y plane also indicates the direction of the rotation of tablet plane around x-axis or y-axis.

Fig. 2 shows a representation of the aragonite tablet orientation distribution obtained according from the micro-beam Laue diffraction patterns variation. The partition between the regions in Fig. 2 (a) is marked with five different colours used to distinguish between adjacent regions. By comparing between Fig.2 (a) and Fig. 1 (b), it is found that, in most cases, within each region (tablet), the distribution of misorientation seems to be approximately uniform but different between regions (tablets). The nacre growth mechanism may partially explain why the tablets have the uniform c-axis orientation but random in a- and b- axis, since the tablets nucleate first, and “expand” until they reach each other [7]. The misorientation in the nucleus will result in the misorientation of each tablet, but orientation will remain almost uniform within each individual tablet. Meanwhile, it is interesting to note that in some tablets variation of misorientation may exist. It seems to display a certain ordered nature, which may have influence on the mechanical properties or strengthening mechanisms.

Fig. 2. Aragonite tablets distribution by micro-beam Laue diffraction patterns. (a) tablets distribution of 13×31
scanned points. (b)-(e) four distinct Laue diffraction patterns

In summary, the results from this study give initial insight into the small misorientation present in the naturally grown impact-resistant structures, such as a green abalone shell. Further investigation is needed of the relationship between crystal (mis)orientation and tablet morphology and strength. This information is essential for improving our understanding of the intricate link between crystallography and mechanical properties of these fascinating systems.

REFERENCES