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Study on microstructure and thermodynamics of nacre in mussel shell

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ABSTRACT

The nacre of mussel shell of *Tellinella asperrima* was analyzed with HRTEM. The results show that the shape of aragonite platelets of the nacre in shell appears irregularly polygon. The thickness of organic matrix layers is rather uneven. There exist mineral bridges in organic matrix interface between two aragonite platelets. The size of the mineral bridge is uneven and it is distributed at random. Many disorderly distributed stacking faults exist within the aragonite tablets. According to XRD analysis, there is a strong preferential orientation of (0 0 2) plane in nacre, simultaneously (0 1 4) plane and (0 1 2) plane also present weak preferential orientations. In addition, the phase transformation was studied by DTA and TG. The result showed that the transition temperature of aragonite (360–380 °C) in the shell is lower than the natural aragonite (450–500 °C) under the influence of organic matrix.

1. Introduction

Analysis indicates that the natural materials are usually inhomogeneous and multi-phases, multi-scale structures, or even porous. The nacre in mussel shell is composed of calcspar or aragonite ($CaCO_3$) (about 95 vol.%) and a small amount of organism (about 5 vol.% or so). Compared with natural mineral aragonite, nacre is with excellent mechanical properties, for example, abalone nacre has a work of fracture about 3000 times greater than that of a single crystal of the pure mineral [1]. That excellent matching between structure and performance of nacre provides a conceptual guidance to the bio-mimetic design of synthetic materials. So the microstructure of nacre has been of major concern, and some achievements have been gained. But up to now the study of its microstructure is not profound. In 1997, Schaffer et al. [2] observed the hole in the organic matrix interface of nacre, and based on this fact they suggested that in the organic matrix interface there might be a number of nano-scale aragonite crystals perpendicular to both upper and lower aragonite platelets, these nano-scale aragonite crystals were referred to as "mineral bridges". However, they could not offer the conclusive evidence of the mineral bridges [3]. In 2002 and 2003, based on the transmission electron micrographs of nacre, Song et al. [3–5] confirmed the existence of mineral bridges in the organic matrix interface. It was proposed that the micro-architecture of nacre should be considered as "brick–bridge–mortar" (BBM) arrangement rather than traditional "brick and mortar"(BM) one, where brick refers to flat polygonal crystals of aragonite, and mortar, the organic matrix interface in nacre, is a biological organic adhesive composed of polysaccharide and protein fibers [3]. But, so far, the most direct proof in favor of mineral bridges is still the only one provided by Song et al., and sub-structure of aragonite tablets is still not thoroughly investigated probably because of observation difficulties. The difficulties in observation maybe owe to that samples are prone to turning into powders under the electron beam bombardment.

Preferential orientation of aragonite crystals in nacre is also a focus of research. Aragonite crystal structure is in monoclinic crystalline form. Most researchers believe that aragonite crystallites only exist one kind of preferential orientation, which is the *c*-axis of aragonite perpendicular to nacreous layer [2,6–8], few authors think that there are other preferential orientations [9,10].

In the present work, direct observations of mineral bridges in the organic matrix interface and sub-structure of aragonite tablets were carried out using high-resolution transmission electron microscopy (HRTEM). The existence of mineral bridges was secondly confirmed, and stacking faults in the aragonite tablets were firstly reported. Preferential orientations of aragonite crystallites in nacre were investigated with X-ray diffraction. Moreover, the phase transformation was studied by thermogravimetric–differential thermal analysis (DTA and TG).

2. Experimental details

2.1. Sample preparation

The shells were from *Tellinella asperrima*, aged 3–4 years of the adult body, and then nacre layer and prismatic layer of air-dried shell were artificially separated with razor. The nacre layer with smooth surface and uniform thickness was used to

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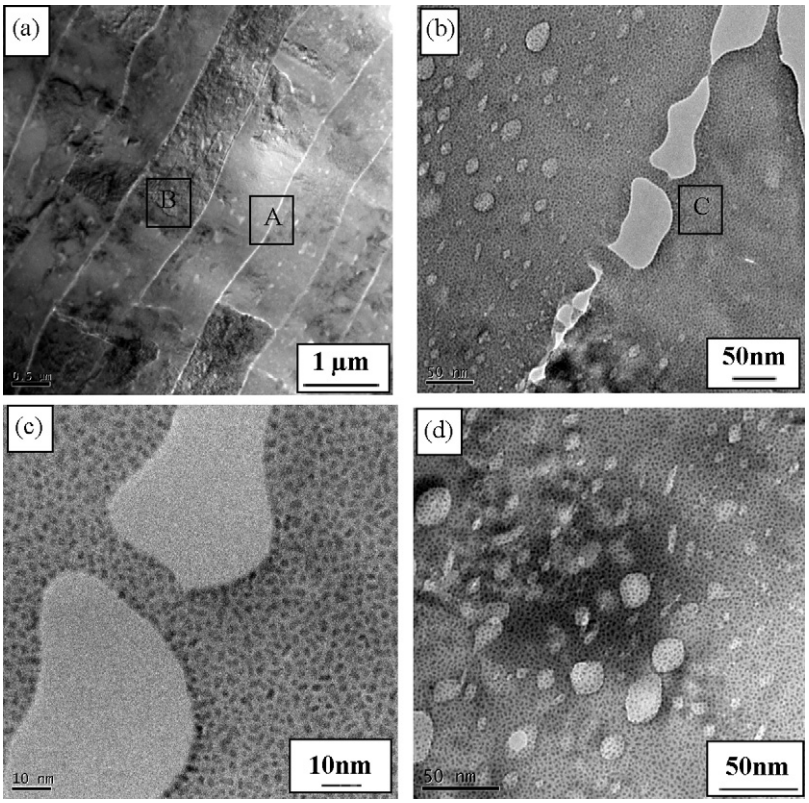

Fig. 1. TEM micrograph of the profile section of the nacre: (a) "brick and mortar" arrangement, (b) mineral bridge and organic sheet (enlarged view of A region in (a)), (c) mineral bridge between two tablets of nacre (enlarged view of C region in (b)), and (d) nano-granules on the tablet (enlarged view of B region in (a)).

prepare testing samples. Some nacre was grinded into fine powder about size less than 45 μm in ball grinder in order that we can investigate the difference of crystallographic orientation of aragonite crystals between broken nacre and unbroken nacre. Nacre was artificially worn thin to about 50 μm and then thinned by ion to prepare the HRTEM observation samples. The samples also needed to be sprayed an extremely thin gold layer on the opposite of observation surface to prevent pulverization under electron beam illumination.

2.2. Experimental conditions

HRTEM observations were performed with a JEM-3010 (JEOL Ltd., Akishima, Japan). Ion beam thinner FISCHIONE-1010 (JEOL Ltd., Akishima, Japan) was used to prepare HRTEM samples.

Philips X'pert MPD Pro X-ray diffractometer (Philips Analytical Help Desk, Holland) was employed to investigate the preferential orientations of nacre. Radiation was Ni-filtered Cu Kα with $\lambda = 1.54068 \times 10^{-10}$ m. Scanning angle was 6–80°.

DTA and TG were performed with a Labsys TG–DTA16 thermal analyzer (Setaram Instrumentation, France). Starting temperature, ending temperature and heating rate were 0 °C, 1000 °C and 10 °C min^{-1}, respectively. N_2 was used as protective gas.

3. Microstructure characteristics of nacre

3.1. TEM micrographs of the profile section of nacre (perpendicular to nacre surface)

TEM micrographs of the profile section of nacre with different magnification times are shown in Fig. 1. Interlocking aragonite tablets stagger in successive lamina and are adhered by organic matrix interface (Fig. 1(a)). In Fig. 1(a), A region (organic matrix interface) was enlarged for viewing, "mineral bridges" were directly

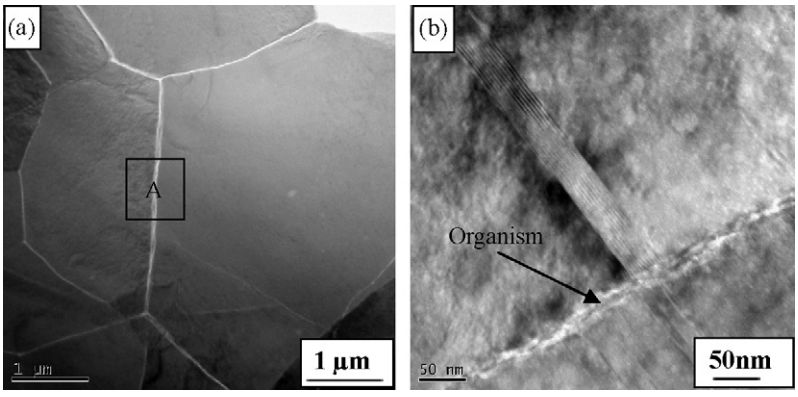

Fig. 2. TEM micrograph of the nacre in a face parallel to nacre surface: (a) polygonal aragonite tablet and (b) organic matrix interface and stacking fault in tablet (enlarged view of A region in (a)).