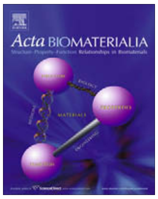
Acta Biomaterialia 6 (2010) 1001–1005

Contents lists available at ScienceDirect

Acta Biomaterialia

journal homepage: www.elsevier.com/locate/actabiomat



A kinetic model of the transformation of a micropatterned amorphous precursor into a porous single crystal

Peter Fratzl [a,*], Franz Dieter Fischer [b], Jiři Svoboda [c], Joanna Aizenberg [d]

[a] Max Planck Institute of Colloids and Interfaces, Department of Biomaterials, Research Campus Golm, 14424 Potsdam, Germany
[b] Institute of Mechanics, Montanuniversität Leoben, Franz-Josef-Strasse 18, A-8700 Leoben, Austria
[c] Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Žižkova 22, CZ-616 62, Brno, Czech Republic
[d] School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02139, USA

ARTICLE INFO

Article history:
Received 4 May 2009
Received in revised form 1 September 2009
Accepted 2 September 2009
Available online 6 September 2009

Keywords:
Amorphous calcium carbonate
Biomineralization
Crystallization
Nucleation and growth
Phase transformation

ABSTRACT

Biogenic single crystals with complex shapes are believed to be generated by the crystallization of an amorphous precursor. Recent biomimetic experiments on the crystallization of calcite via amorphous-to-crystalline transition point to the fact that the transformation kinetics may be controlled by the micropattern and the macroscopic shape of the amorphous precursor phase. Here we analyse a simple kinetic model, based on thermodynamic considerations, showing that the presence of cavities in the micropatterned precursor phase might interfere with the transformation process and control its kinetics. The size of the cavities couples to the total surface energy and, hence, to crystal nucleation and growth, while the spacing of the cavities, as compared to the typical diffusion path, controls the possible nucleation of competing crystals.

1. Introduction

Many biological crystals are grown by the transformation of amorphous precursor phases [1–8]. For example, it has been shown that amorphous calcium carbonate (ACC) transforms into calcite or aragonite in the skeletons of echinoderms and molluscs, and that amorphous iron oxides transform into magnetite in chiton teeth. The advantage of this type of processing is that it apparently allows the growth of single crystals with very complex shapes [9,10]. It has also been argued that amorphous precursor phases substantially modify the nucleation process as several subcritical nuclei may coexist, survive and eventually coalesce within a single amorphous precursor particle [11–17]. Recently, it has become possible to stabilize amorphous calcium carbonate as a precursor of calcite crystals in laboratory conditions and to initiate controlled crystallization of large single crystals [17–21].

One of the challenges in understanding the kinetics of this transformation is to rationalize the effect of the volume change between ACC and calcite, which is much denser. Hence, crystallization of ACC is not possible without considerable mass transport at the nano- and micrometer levels. It is quite surprising that the formation of a large single crystal is actually possible under these conditions. One would suspect that the negative volume jump from ACC to calcite would disrupt the crystallization front and the remaining ACC pool, making the growth of a single crystal difficult. Indeed, the formation of polycrystalline calcite is observed when a large plate-like ACC template transforms, even starting from a single artificial nucleation site [18]. However, when the ACC template is pre-structured by a periodic array of holes (cavities) in the plate-like template, a large single crystal may grow under similar conditions [18,22]. As shown in Fig. 1, large single crystals with periodic arrays of holes occur in natural systems and can be grown in the laboratory. The size and spacing of these holes seem to play a major role in the kinetics of the crystallization process, since a single crystal is formed only when the spacing of the holes is sufficiently small. The size of the holes has been observed to increase during crystallization, clearly compensating for the volume decrease from ACC to calcite. All these experimental observations suggest an important role of geometric constraints in the transformation process from an amorphous precursor to a single crystal, but the physical nature of this influence is still uncertain.

2. Problem formulation

In this paper, we carry out theoretical investigations of the influence of geometric constraints on a phase transformation process with a considerable volume jump. The hypothesis that cavities in the precursor reduce the mechanical stresses arising from the

---

* Corresponding author. Tel.: +49 331 567 9401; fax: +49 331 567 9402.
E-mail addresses: fratzl@mpikg.mpg.de, fratzl@mpikg-golm.mpg.de (P. Fratzl), mechanik@unileoben.ac.at (F.D. Fischer), svobj@ipm.cz (J. Svoboda), marina@seas.harvard.edu (J. Aizenberg).

1742-7061/$ - see front matter © 2009 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.actbio.2009.09.002

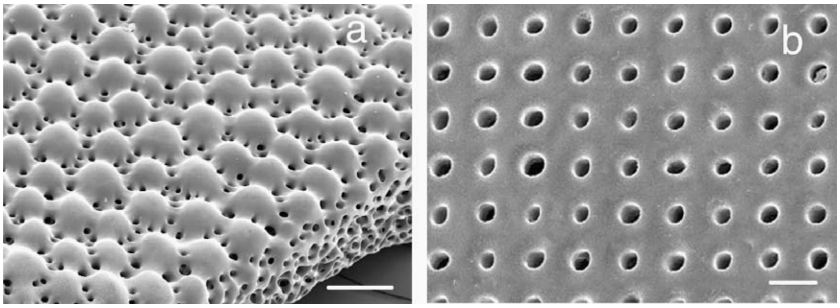


Fig. 1. (a) Scanning electron micrograph (SEM) of a part of the skeleton of a brittlestar *Ophiocoma wendtii* (Ophioroidea, Echinodermata). The entire structure (the mesh and the array of microlenses) is composed of a single calcite crystal used by the organism for mechanical and optical functions [9]. (b) SEM of a sample micropatterned single calcite crystal fabricated by transformation of an amorphous precursor. The holes were pre-existing in the precursor and grew during the transformation process [18]. Bar = 100 and 10 μm in (a) and (b), respectively.

volume change [18] is not likely to be true, because the presence of holes leads to stress concentration and increases the risk of failure initiation, rather than preventing the disruption between the parent ACC phase and the crystal [23]. To avoid this, the parent phase has to be sufficiently ductile to allow for accommodation of the deformation without stress concentrations. The latter condition is fulfilled for the water-rich ACC phase, which is quite soft and deformable compared to calcite. Moreover, recent experiments on the controlled crystallization of ACC show that, indeed, ACC rearranges considerably around growing crystals to form halos [19].

Here we analyse the possible influence of holes on the kinetics of the transformation of ACC to calcite within a simple theoretical model. We find that the presence of cavities in the micron range can inhibit calcite nucleation and promote the growth of a single crystal from a sufficiently large artificial nucleus. We show that the time required for the crystal surface to bridge the distance a between two holes scales as a^2, which needs to be compared to the time for nucleation of a competing crystal. Hence, a single-domain crystal will only form when the distance between holes is small enough to prevent secondary nucleation.

The model studied is (quasi-) two-dimensional, consisting of a planar, perforated layer (with a large thickness d) of ACC with the starting configuration shown in Fig. 2. The ACC layer contains a periodic array of circular holes with radius ρ_W and the initial radius ρ_{W0}, distributed in a square lattice with the unit cell dimension of a. During a diffusive transformation process the phase ACC transforms into crystalline calcite (CC) and liquid water (W). The molar fractions, molar volumes and molar Gibbs energies of individual phases are listed in Table 1.

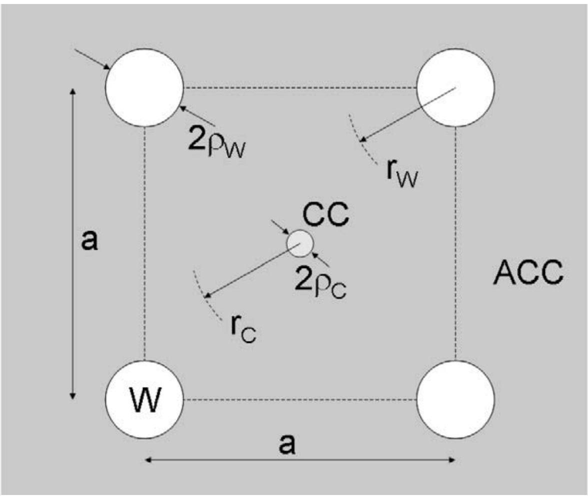


Fig. 2. Sketch of the configuration of holes (W) and the calcite nucleus (CC) in the ACC plate. The holes with radius ρ_W (with ρ_{W0} being its initial value at the start of crystallization) are arranged on a square lattice with spacing a. The radius of the calcite nucleus is ρ_C, and the distance from the centre of the calcite nucleus and of the holes is r_c and r_W, respectively.

3. Problem solution

We assume that, at the beginning of the phase transformation, a calcite nucleus grows to an initially very small circle around the centre with radius ρ_C, while the holes increase their radius from ρ_{W0} to ρ_W in order to compensate for the decrease of the volume of calcium carbonate during the transformation from the ACC to the calcite phase. We postulate that the accommodation of the transformation strain, arising from significant shrinking, can be realized by the viscous behaviour of the ACC. Without this property of the ACC, transformation stresses would accumulate at the interface between calcite and ACC, which must lead either to a stopping of the transformation or to a fracture of the specimen.

When the calcite crystal grows from 0 to ρ_C and the holes grow from ρ_{W0} to ρ_W, we can write two conservation relations – one for the calcite and one for the water.

The first one expresses the conservation of calcium ions, with x being the molar fraction of water in ACC:

$$\frac{M_C}{d} = \frac{\pi\rho_C^2}{\Omega_C} = (1-x)\frac{M_A}{d} = (1-x)\frac{\pi\rho_C^2 + \pi\rho_W^2 - \pi\rho_{W0}^2}{\Omega_A}, \tag{1}$$

where it is assumed that M_A moles of the amorphous phase is being transformed into M_C moles of calcite and that the layer thickness d remains roughly unchanged during the crystallization (that is, the mass redistribution is supposed to mainly occur within the plane of the layer and not in the third dimension). This equation can be transformed to

$$\frac{\rho_W^2 - \rho_{W0}^2}{\rho_C^2} = \frac{\Omega_A}{(1-x)\Omega_C} - 1 \equiv \alpha, \tag{2}$$

where the parameter α describes the relative volume decrease when a given amount of calcium atoms transforms from ACC to calcite. The quantities Ω_A and Ω_C are the molar volumes of ACC and calcite (see Table 1).

The second conservation relation defines the total number M_W of moles of water which had to leave the amorphous phase during the transformation process:

$$\frac{M_W}{d} = x\frac{M_A}{d} = \frac{x}{1-x}\frac{\pi\rho_C^2}{\Omega_C}. \tag{3}$$

The change ΔG in the total Gibbs free energy G (within the unit cell in Fig. 2) due to the nucleation of a calcite crystal of size ρ_C is given