

Fibrillation and Morphological Evolution of Alkaline-Earth Carbonates with Silicate

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Calcium, strontium and barium carbonates having unique non-crystallographic shapes, such as spicule aggregates and twisted ribbons, were obtained in silica gel or silicate solution at high pH. The shape of the carbonate crystals changed from the regular symmetry into non-crystallographic morphology with increasing pH. The carbonates prepared at high pH were found to be composed of small crystalline units covered with silicate. We assume that the selective adsorption of silicate ions on the carbonate surfaces induces fibrillation of the crystals and that the unique aggregates are formed through self-organization of the crystalline subunits.

Key words: self-organization, morphology, carbonate crystal, silica gel, biomineralization

1. INTRODUCTION

Self-organization of engineered crystals with unique non-crystallographic morphology is a feature of biomineralization. Organic molecules adsorbed on crystals affect to crystallochemical specificity of biomineralization.¹ Identifying this biological ability is essentially important for novel fabrication of advanced materials. The influences of organic additives on calcium carbonate crystallization have been reported.²⁻⁴ Crystal growth was also modulated with addition of several inorganic ions.⁵⁻⁸ However, the specific morphological evolution of biominerals through self-organization has not been clarified.

García-Ruiz et al.^{9,10} reported that precipitates formed by a reaction of alkaline-earth metal cations and carbonate anions in silica gel showed non-crystallographic shapes, such as spiral and twisted ribbons. These unique shapes inspire biological products although the microstructure of the unique shapes and the formation mechanism are still unknown. Investigation of this morphological evolution is associated with understanding self-organization of inorganic materials on the biomineralization. From this view point, this paper reports the morphological evolution, the microstructure and the composition of alkaline-earth carbonate crystals grown in silica matrix at various pH over 6-13. We found that the formation of the non-crystallographic morphology is attributable to self-organized assembly of small crystal subunits covered with silicate.

2. EXPERIMENTAL PROCEDURE

Silicate solutions containing carbonate ions (0.05 M) were prepared by mixing 14.9 g sodium metasilicate nonahydrate with 200 g purified water and a certain amount of sodium carbonate. The precursor solutions which were adjusted over pH 6-13 with hydrochloric acid gradually changed into sol

and then gel. Gelation did not occur in the high pH region above 10.5. Calcium chloride, strontium chloride or barium chloride dihydrate solution at a concentration in 0.1-1.0 M was poured onto the silica gel or the silicate solution. The silica matrix loaded with the calcium, strontium or barium solution was kept at room temperature.

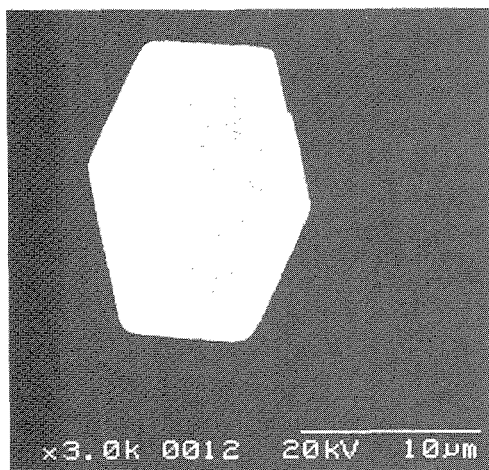
Glass slides were immersed in the solutions before gelation. The precipitates deposited on the glass plates were washed with water and then dried at 60 °C.

The products were observed with a scanning electron microscope (SEM, Hitachi S-2150) and a field-emission scanning electron microscope (FE-SEM, Hitachi S-4700). The composition of the products was analyzed with electron probe microanalysis (EPMA, Shimadzu 8705) and energy dispersive X-ray microanalysis (EDX) equipped on the FE-SEM. X-ray diffraction (XRD) measurements were performed on a Rigaku RAD-C diffractometer using CuK α radiation.

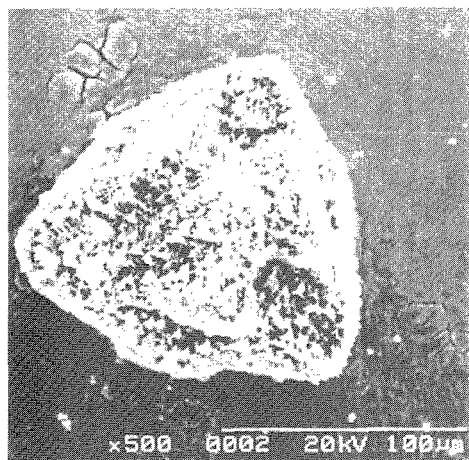
3. RESULTS AND DISCUSSION

White precipitates were observed in the silica matrix (silica gel or silicate solution) in all the pH region after being kept for several hours. Silica gel covering the products stuck on glass substrates was easily removed by washing with water. Using this technique, we directly observed the microstructure of the precipitates without dissolution of silica gel. Precipitates induced with calcium solution in silica matrix at < pH 9 were identified to be calcite, while the mixture of calcite and aragonite was obtained at > pH 10. Products with strontium and barium solutions were aragonite-type carbonate crystals regardless of pH of the matrix. On the other hand, the morphology of the precipitates was drastically influenced by pH although the concentration of calcium, strontium or barium chloride hardly affected the shapes. The

precipitates formed in silica gel at the low pH had regular crystallographic symmetry. Normal calcite rhombohedra, comprising six smooth {104} faces, was observed around pH~7 (Figures 1(a)). Hexagonal rods of barium carbonate (Figure 2(a)) were formed around pH~7. Aragonite-type crystals are known to be commonly hexagonal in shape. However, the morphology of the carbonate crystals changed from the regular morphology to non-crystallographic shapes with increasing pH of the silica matrix. Spicule aggregates of calcium carbonate were formed around pH 10-11 (Figures 1 (b)). Electron diffraction clarified that this unique precipitates also consisted of calcite crystals. Twisted ribbons of barium and strontium carbonates were formed above pH 9.5 (Figure 2(b)). These precipitates were identified to be aragonite-type crystals.

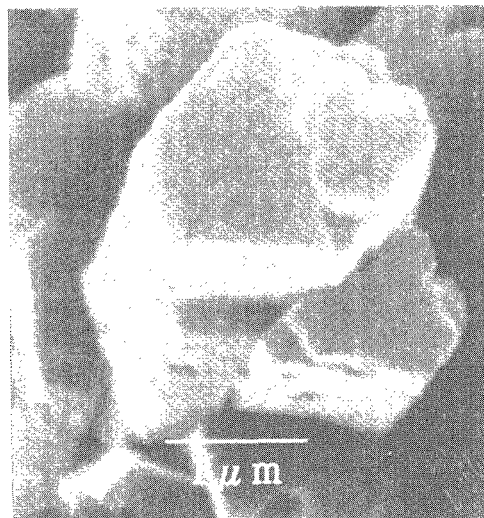


(a)

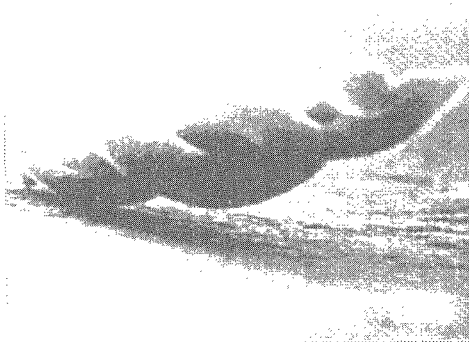


(b)

Figure 1 SEM images of calcium carbonate formed at pH ~7 (a: regular rhombohedra) and pH ~10 (b: spicule aggregate).



(a)



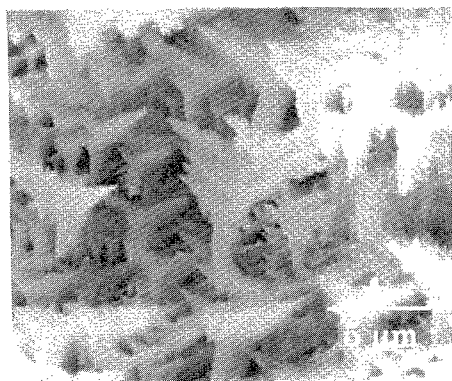
(b)

Figure 2 SEM images of barium carbonate formed at pH ~7 (a: hexagonal rods) and pH ~10 (b: twisted ribbon).

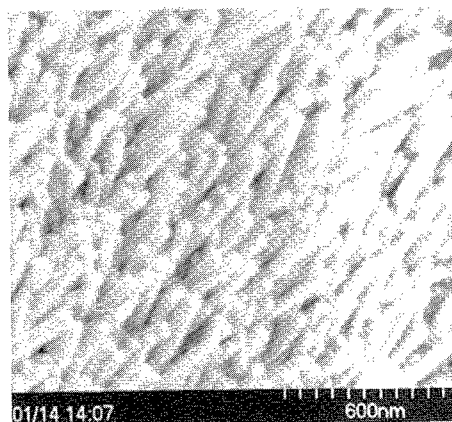
The FE-SEM observation clarified that the unique shapes of carbonates were composed of small crystalline components. Spicule aggregates of calcium carbonate consisted of small subunits (Figure 3(a)). Needle-like nanocrystals which aligned perpendicularly to the surface were observed on the twisted ribbons of strontium and barium carbonates (Figure 3(b)).

Although García-Ruiz et al.^{9,10} has reported the formation of the non-crystallographic morphology in silica gel, the evolution of the morphology and the microstructure with increasing pH was hardly shown. Moreover, the formation mechanism is still unknown. We found that the adsorption of silicate ions is associated with the formation of the non-crystallographic morphology. The amount of silicon

covering the aggregates increased with increasing pH of the silica matrix. The solubility of silicate ions steeply increases above pH-8¹¹. Cyclic tetramers ($\text{Si}_4\text{O}_6(\text{OH})_6^{2-}$, $\text{Si}_4\text{O}_8(\text{OH})_4^{4-}$) are reported as soluble silicate anions in high-pH solutions¹². Thus, the increase in the amount of silicon on the carbonate crystals is ascribed to the adsorption of the silicate anions on the crystal surface. The crystal planes parallel to the c-axis of calcite and aragonite-type crystals specifically adsorb the cyclic tetramers because the distance between carbonate ions on the planes is similar to that between the anionic sites of the silicates. The adsorption usually suppresses the growth of crystals and perturbs the morphology. The morphological change of calcium carbonate was reported to be induced with the adsorption of several organic molecules.²⁻⁴ On the other hand, the growth of the carbonate crystals is entirely prevented by silicate ions because the adsorbed silicates are easily polymerized with dehydration. Thus, the adsorption of silicate ions also results in the fibrillation of the carbonate crystals.



(a)



(b)

Figure 3 FE-SEM images of a spicule aggregate of calcium carbonate (a) and a twisted ribbon of barium carbonate (b).

The small subunits (Figure 3 (a) and (b)) composing the non-crystallographic calcite and aragonite-type crystals showed almost the same orientation. This result suggests that the unit crystals have crystallographic connections with each other. The adsorption of silicate ions suppresses continuous growth and then promotes branching. The crystalline subunits assembled with weak crystallographic interactions were formed through the fibrillation and the branching. The assembled crystalline units covered with silicate ions are flexible and easily deformed during the crystal growth. Finally, a high concentration of silicate ions at high pH induces the production of the crystal aggregates having the non-crystallographic morphology. We presume that the unique morphology is associated with self-organization of unit crystals during the growth. However, further investigation is required to clarify the mechanism of the evolution of the complex shapes.

4. CONCLUSIONS

Non-crystallographic shapes, such as spicule aggregates and twisted ribbons, of carbonate crystal aggregates were formed in silica matrix at high pH. The aggregates were found to be composed of small carbonate crystals. Since the fine crystals were covered with silicate, the selective adsorption of silicate ions on the carbonate surfaces causes fibrillation of the crystals. Self-organized assembly of the fine crystals covered with silicate ions is assumed to result in formation of the unique morphology.

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