

MIS020-P01

会場: コンベンションホール

時間: 5月24日 10:30-13:00

ゲーサイト表面のドメイン構造と欠陥の生成機構 Formation mechanism of domain structure and defect of goethite surface

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Goethite (alpha-FeOOH) is one of the most common iron (oxyhydr)oxide minerals in surface environment of Earth and has huge specific surface area due to the small particle size. The surface of goethite plays an important role in many chemical reactions, e.g., adsorption, dissolution and precipitation, and thus their mechanism and kinetics are studied in detail using synthetic goethite. However goethite occurring in natural environment shows wide range of crystallinity (Kuhnel et al., 1975) and it is known that many properties, e.g. *a*-dimension of the unit cell and OH bending mode, are affected by the crystallinity (Schwertmann et al., 1985). Goethite with low crystallinity shows multidomain structure and weak hydrogen bonds owing to the -OH defects in the crystal structure and those characteristics accelerate the dissolution and adsorption rates (Strauss et al., 1997). In this study, we investigate the surface morphology and the ratio of surface hydroxyl group to oxygen, $[-OH]/([-O] + [-OH])$, of goethite with varying crystallinity and discuss the formation mechanism of multidomain structure and OH defects.

Goethite in this study was synthesized using ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) and potassium hydroxide (KOH) as starting materials, according to Schwertmann et al. (1985). The dark brown precipitate, which is amorphous ferric oxide called ferrihydrite, was aged for 70 days at 4 °C (G-04), 30 days at 30 °C (G-30), 10 days at 50 °C (G-50) and 3 days at 70 °C (G-70). All products were washed with pure water, dried in nitrogen atmosphere and identified as goethite by powder XRD analysis. The morphology of these goethite were observed using AFM and specific surface area were measured with 11-points BET method. X-ray photoelectron spectroscopy (XPS) was employed to analyze the ratio of surface hydroxyl groups to surface oxygen.

AFM observations revealed that all goethites have acicular morphology, however, goethite aged at high temperature has larger particle size (> 1000 nm), higher aspect ratio and monodomain structure. On the other hand, goethite aged at low temperature has smaller particle size (< 200 nm), lower aspect ratio and multidomain structure. This observation well agrees with TEM observation by Schwertmann et al. (1985). XPS analysis revealed that the ratio of surface hydroxyl group to oxygen, $[-OH]/([-O] + [-OH])$, was higher for the goethite aged at higher temperature.

Transformation of ferrihydrite into goethite proceeds in three stages (Cornell et al., 1989; Yuwono et al.): (1) crystallization of goethite nanoparticles from ferrihydrite nanoparticles, (2) oriented attachment of goethite nanocrystals and (3) development of crystal morphology by aging. In aging at high temperature, ferrihydrite nanoparticles crystallize rapidly and completely, and thus oriented attachment occurs without misalignments. As a result, goethite aged at high temperature has monodomain structure and high aspect ratio. On the other hand, in lower temperature, ferrihydrite crystallizes into goethite nanoparticles slowly and incompletely, hence aggregation of the goethite nanoparticles has many misalignments. The multidomain structure, OH defects and low aspect ratio of goethite aged at low temperature arise from the misalignments within the aggregate of nanoparticles as a precursor of aged goethite.

キーワード: 結晶性, 結晶形態, 粒径, 原子間力顕微鏡, X線光電子分光
Keywords: crystallinity, crystal morphology, particle size, AFM, XPS

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DNA ナノ構造体形成実験とその結晶成長学的考察 DNA nano-structure formation and the interpretation based on crystal growth theory

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The DNA molecule is now attracting attention as a new self-assemble material. The reason why DNA is used for self-assembly is that DNA molecule has calculation capability. Many nanostructures have been produced using DNA, for example, DNA tile (Winfree and Seeman, 1998). DNA tile is a complex molecule, which is composed of some single strand DNA (ssDNA). Each tile has some sticky ends (a part of some exposed bases). The complementary sticky end spontaneously makes hydrogen bond and grow to large ordered structure (DNA tile crystal) as the solution cools down. This process is termed as self-assembly, in other words, crystallization. Although DNA tile has potential as computer, there are some problems. The most important matter is presence of error (misfit crystallization). In order to reduce this error, many types of DNA tiles have been designed. However, it is difficult to completely prevent the assemble error. For synthesis of DNA tile crystal without the assemble error, we carried out experimental study of DNA tile formation and interpreted the result based on crystal growth theory.

First, we chose T-motif as DNA tile, which is able to grow on the electrically-charged Mica surface like two dimensional crystal, and measured its growth rate using DNA origami as a seed crystal with atomic force microscopy. The growth rate of T-motif crystal on Mica substrate was about 4.30 [monomers/minute].

In the second experiment, we observed T-motif crystals synthesized on the Mica surface for various conditions (temperature and concentration). We found that the nucleation temperature of the T-motif crystal was about 41.5 [deg. C.], which did not depend on the concentration significantly in a range of 2~10 [nM]. From this result, we assumed that the T-motif crystal growth can be considered to be melt growth. In order to understand the growth mechanism, we calculated the step free energy β [J/m] and melting point T_m [deg. C.] under the assumption that the number density of crystals on the Mica surface is proportional to the two-dimensional nucleation rate. When the melting point is assumed to be 50 [deg. C.], the calculated step free energy was about 4.21×10^{-13} [J/m]. The calculated step free energy of T-motif crystal is similar to that of Lysozyme crystal (8.9×10^{-13} [J/m]).

We also observed the morphological change of T-motif crystals depending on the growth condition. In the highest supersaturation condition in this study (T-motif concentration is 10 [nM] and temperature is 38 [deg. C.]), the morphology of the T-motif crystal was similar to dendrite crystal. In other cases, the morphology was found to be polygonal shape. The reason why the T-motif crystal becomes dendritic in the highest supersaturation condition is considered to relate to the thermal stability of the sticky end binding. In low supersaturation, many T-motif units bind only at a site with two sticky ends. In contrast, in the highest supersaturation, the T-motif unit can bind to anywhere. We calculated the difference of Gibbs free energy in two conditions; one match bond of sticky end or two matches. We found that when the driving force exceeded the critical point, the T-motif crystal has possibility to be formed as dendrite. Using the critical driving force, we calculated the temperature at which the T-motif dendrite crystal was formed. In this calculation, the temperature of dendrite formation is 41.8 [deg. C.] when the melting point is assumed to be 50 [deg. C.]. On the other hand, experimental result shows that T-motif dendrite form in 38 [deg. C.]. The inconsistency between the theory and the experiments should be resolved in the future, however, our study is an important first step to describe the growth mechanism of the T-motif crystal based on the theory of crystal growth from melt phase.

キーワード: DNA タイル, 結晶成長

Keywords: DNA tile, Crystal growth

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リン酸第8カルシウムのモルフォロジー形成時における中間生成物の役割 The morphological relationship of octacalcium phosphate and its precursor: the role of intermediate phase

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Octacalcium phosphate (OCP) is the precursor of hydroxyapatite (HAP) which is main component of human tissue. HAP crystals which form through OCP are pseudomorph of OCP. Thus, the investigation of OCP morphological decision is connected with the later phase, HAP morphological decision. In around neutral pH solution, amorphous calcium phosphate (ACP) is precipitated as an initial solid phase at supersaturated calcium phosphate solution. Wherein, we investigated the formation process of characteristic morphology of OCP from ACP in solution.

We prepared 1 mol/L CaCl₂ and 0.5 mol/L KH₂PO₄ solutions which were also buffered by tris amino methane, and 0.15 mol/L tris amino methane-HCl buffer solution. These three solutions were gently blended without stirring to observe the morphological connection between initial phase and later phase through the materials evolution of calcium phosphates precipitations in solution by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). (The total concentration is Ca = 0.075 mol/L, PO₄ = 0.045 mol/L, tris amino methane = 0.015 mol/L, 32 °C, initial pH = 7.7) Immediately after blending, white indeterminate precipitates were emerged and formed gel-like structure which was maintained for 40 minutes after blending. The solution pH was gradually decreasing around 4 until 40 minutes later. In FE-SEM and TEM observation, the gel-like structure was consisted of sphere-like ACP particles with 100 nm in diameter and ACP spherulites with 3-20 micro meter in diameter. In proceeding time, fiber-like beta-tri calcium phosphate crystals (TCP) were emerged in gel-like structure and ACP sphere particles were vanished. 3 minutes later, ACP spherulites transformed through TCP like phase. 6-12 minute later, the TCP like phase spherulites transformed spherulites which composed of both of single OCP crystal and TCP polycrystals. TEM dark field image showed OCP and TCP domains were mingled. Finally, the spherulites transformed into single OCP crystals with maintain their whole spheritic morphology until 40 minutes later. These observations suggested that OCP is pseudomorph of ACP. In below 7 pH solution, it suggested that through TCP like phase, morphology of OCP crystals was maintaining initial phase morphology, ACP.

キーワード: リン酸第8カルシウム, モルフォロジー, 前駆体, 相転移, 仮晶

Keywords: octacalcium phosphate, morphology, precursor, phase transition, pseudomorph

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二酸化炭素固定化に向けた水酸化カルシウム結晶の溶解・成長速度測定 In situ measurement of dissolution and growth velocities of $\text{Ca}(\text{OH})_2$ for CO_2 trapping

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昨今地球温暖化問題が取りざたられる中, 対策技術として CCS (Carbon dioxide Capture and Storage) が注目を浴びている. CCS は二酸化炭素を回収後, 地中や海中に貯蔵・固定する技術を指すが, その固定法の 1 つに鉱物固定が挙げられる. これは二酸化炭素をカルサイトなどの地球上で安定な鉱物として地中や海中に固定化するもので, 二酸化炭素の長期間の安定貯蔵が期待されている. カルサイトを生成する 1 つの反応として, 水酸化カルシウム結晶に炭酸イオンを含む溶液を反応させ, カルサイトを生成するという方法がすでに考えられている (Lackner et al., 1995). しかし水酸化カルシウム結晶がカルサイトに置換・成長する速度は分かっておらず, またこの反応の出発物質である水酸化カルシウム結晶の成長・溶解速度も分かっていない. そこで本研究はカルサイト化による二酸化炭素固定の速度を解明するために, 反応に関わる重要な物質である水酸化カルシウムの (001) 面の成長・溶解速度を その場 観察によって求めることを目的とした.

面成長・溶解速度測定には位相シフト干渉計を用いた. 位相シフト干渉計は垂直分解能 $w/(2n \times 255) \text{ nm}$ ($w = 532 \text{ nm}$, $n = 1.333$) を持ち, nm/s の成長・溶解速度を測定することができる. 0.25 M CaCl_2 溶液, 0.50 M NaOH 溶液, 2.0 M NaCl 溶液と純水を混ぜ合わせることで, 過飽和度を $-0.46 \sim 0.29$ の範囲で変化させながら, 水酸化カルシウム結晶 (001) 面の結晶成長・溶解速度を測定した.

面成長速度の過飽和度依存性より, 本実験で採用した過飽和度の範囲における水酸化カルシウム結晶の成長様式は多核成長であることが推測された. 多核成長時に形成される二次元核の縁の単位長さ当たりのステップエッジエネルギー $= 1.093 \times 10^{-11} \text{ J/m}$ を初めて求めることができた. この値は, 先行研究 (Teng et al., 2000) で得られたカルサイト (10-14) 面の面成長速度から求めたステップエッジエネルギーよりも小さい. これはカルサイト (10-14) 面よりも低い過飽和度領域において多核成長をする理由であると考えられる.

さらに, 鉱物による二酸化炭素固定メカニズムの解明に向けて, 水酸化カルシウム結晶の面溶解速度の測定結果に基づき, 水酸化カルシウム結晶とカルサイト共存系において, 水酸化イオン濃度, 炭酸イオン濃度一定の条件のもとで Ca イオン濃度 (過飽和度) を変化させた時の, 水酸化カルシウム結晶の溶解挙動について推測することができた. 共存系では, 上の条件のもと, 水酸化カルシウム結晶, カルサイトに対してどのような過飽和度条件を想定しても, つまりカルサイトにとって未飽和な条件を設定しても水酸化カルシウム結晶の溶解に伴う, Ca イオンの供給によって, カルサイトがいずれは成長に転じるということを推測できた. つまり, 共存系であれば二酸化炭素は必ずカルサイトとして固定されると予想される.

本研究では水酸化カルシウム結晶の (001) 面成長・溶解速度の過飽和度依存性を測定することに初めて成功し, 多核成長時の二次元核形成におけるステップエッジエネルギーを求めることができた. また, 水酸化カルシウム-カルサイト結晶共存系においては, どのような過飽和度条件であっても, いずれはカルサイトが成長することが推測できた. 以上の結果から, 水酸化カルシウム結晶を用いた二酸化炭素の固定化は十分に可能であり, 今後の CCS での鉱物固定では, 水酸化カルシウム結晶は重要な物質の 1 つであることが結論付けられた.

キーワード: 水酸化カルシウム, 炭酸カルシウム, 鉱物固定, 多核成長

Keywords: calcium hydroxide, calcium carbonate, mineral trapping, multi-nucleation

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二酸化炭素固定化に向けた結晶成長研究 Carbon Sequestration

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空気中の炭酸ガス固定化

キーワード: 炭酸ガス固定, 結晶成長, 溶解

Keywords: Carbon Sequestration, Crystal Growth, Dissolution