

## ガス中蒸発法におけるナノ粒子生成過程の高速偏光“その場”観察 High-speed polarized in-situ observation in a nucleation process of nanoparticles produced by the gas evaporation method

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The gas evaporation method has been investigated for more than half a century since the Kubo effect was reported (1962). There have been many studies on the produced nanoparticles mainly using a transmission electron microscope, which have elucidated the different physical properties of nanoparticles from those in bulk. On the other hand, there have been almost no reports on nucleation in smoke related to crystal growth. Recently, we achieved in-situ observation of the nucleation process in smoke using a double-wavelength Mach-Zehnder-type interferometer, which can determine the temperature and pressure at the nucleation simultaneously. A series of experiments clearly showed that smoke particles condense homogeneously only in a very high supersaturated environment [1-3]. In a preliminary experiment using tungsten trioxide, the smoke particles condensed with a degree of supersaturation as high as  $\sim 10^6$ . In this process, since evaporant is continuously supplied into the surrounding of the evaporation source, the flow of smoke after the nucleation and growth of nanoparticles has been simply considered as a consecutive process. The nucleation and growth of smoke particles should be a rapid process (ms order) due to high supersaturation, so the concentration of the evaporated vapor drastically decreases. However, the details of the formation process remain unknown.

In this study, we attempted to visualize the nucleation of nanoparticles and motion of smoke using a high-speed polarization image sensor (Photron Inc.) to clarify the details of the nucleation process of smoke particles. Since the sensor itself has pixels with micro-polarizers, a phase shift interferogram can be obtained in less than a millisecond because of the lack of mechanical movement free, and can therefore be applied to rapid phenomena such as nucleation in vapor phase. Here, we show the preliminary results of homogeneous nucleation of tungsten oxide from vapor phase.

[1] Y. Kimura, H. Miura, K. Tsukamoto, C. Li, T. Maki, Interferometric in-situ observation during nucleation and growth of  $WO_3$  nanocrystals in vapor phase, *Journal of Crystal Growth*, 316 (2011) 196-200.

[2] Y. Kimura, K. Tsukamoto, Interferometric observation of temperature distributions in the smoke experiment, *J. Jpn. Soc. Microgravity* 28 (2011) S9-S12.

[3] Y. Kimura, K. K. Tanaka, H. Miura, K. Tsukamoto, Direct observation of the homogeneous nucleation of manganese in the vapor phase and determination of surface free energy and sticking coefficient, *Crystal Growth & Design*, 12 (2012) 3278-3284.

キーワード: 核生成, 偏光高速カメラ, その場観察

Keywords: Nucleation, High-speed polarized camera, in-situ observation

## フルイド反応 TEM を用いた炭酸カルシウム核生成過程の TEM 中 “その場” 観察 In-situ observation of nucleation process of calcium carbonate by the fluid-reaction TEM

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Recent studies have reported achievements of in-situ observation of the nucleation and crystallization studies using transmission electron microscope (TEM), and several new perspectives for non-classical pathway of crystallization [1-4]. Calcium carbonate generates a lot of attention because of complex nucleation due to appearance of various polymorphs in addition to availability for industrial materials such as paper and paint, and reservoir of carbon dioxide, and biomineralization. We also focus on the calcium carbonate in view of selection of polymorph in nucleation process. In case of nucleation from relatively higher supersaturated solution, nucleation of amorphous phase prior to crystalline phase has been known [5,6]. Kawano et al. have been reported an in-situ observation of solution-mediated phase transition from amorphous phase into crystalline phase under optical microscope [6]. The Ostwald law of stages has been believed to occur in many cases. Contribution of prenucleation cluster, which was confirmed by using the cryo-TEM [8], to the nucleation has also been reported [7]. However the generality or solution condition to take these processes is still not obvious.

Now, we have performed energetically a project to observe crystallization and dissolution processes in an aqueous solution using ionic liquid instead of water or the "Poseidon" (Protochips Inc.), which is a sample holder having a liquid cell for TEM observation. We call our TEM fluid-reaction TEM (FR-TEM), which is able to perform crystallization experiments in a solution including both methods. Here, we have been tried to observe whole the process of crystallization of calcium carbonate via amorphous phase using fluid-reaction TEM and actually observed a solid-state phase transition from amorphous phase into a crystalline phase by in-situ observation.

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キーワード: フルイド反応透過電子顕微鏡, その場観察, 炭酸カルシウム, 核生成

Keywords: Fluid-reaction TEM, In-situ observation, Calcium carbonate, Nucleation

## “Poseidon”を用いた溶解過程のTEM中“その場”観察実験 In-situ TEM observation of dissolution processes in aqueous solutions using “Poseidon”

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Recently, we started a new project to observe crystallization and dissolution processes of crystals in a solution using two different methods under transmission electron microscope (TEM). To overcome the difficulties to introduce a solution into a TEM, Kimura et al. used ionic liquid to avoid evaporation of a solvent in the high-vacuum of a TEM [1]. As the result, several new insights were found: solubility-independent formation of polymorph; crystals do not dissolve smoothly but in a fluctuating manner; and new crystals form even in a totally dissolving system. Another advantage of this method is that the growing crystal does not have a hydrated layer on their surface. It has been believed that dehydration process has a largest potential barrier to incorporate a unit cell into the crystal. However, no one ever visualized the process and it has been totally veiled. The water free experiment using an ionic liquid may give us a new perspective on the dehydration process by comparison with experiments in general aqueous solutions. Now, we are forwarding a project to observe crystallization and dissolution processes in an aqueous solution in atomic-scale using the “Poseidon”, which is a sample holder having a liquid cell for TEM observation. We call our TEM fluid-reaction TEM (FR-TEM) including both solution growth experiments using an ionic liquid and the Poseidon.

Poseidon (Protochips Inc.) give us the opportunity to visualize the three-dimensional process with several advantages compared with previous works using an atomic force microscope, which is able to observe only two-dimensional, and an optical microscope, which has much less lateral resolution. Growth and dissolution processes at the first top layer (surface) of a crystal have been energetically studied long time using these tools. However, the detail process in atomic scale has been observed very limited. Therefore, the aims of our project is understanding of three dimensional nucleation including Ostwald law of stages based on phase determination by electron diffraction, determination of very slow dissolution rates, and dissolution process in terms of an influence of defects. Here, we will show the first pictures about the movements of nanoparticles and dissolution of amorphous silica and crystalline silicate samples.

[1] Kimura, Y., Niinomi, H., Tsukamoto, K. & Garcia-Ruiz, J. M. In-situ live observation of nucleation and dissolution of sodium chlorate nanoparticles by Transmission Electron Microscopy. *J. Am. Chem. Soc.*, DOI: 10.1021/ja412111f. (2014).

キーワード: フルイド反応透過電子顕微鏡, 溶解, その場観察  
Keywords: Fluid-reaction TEM, Dissolution, In-situ observation

## モンモリロナイトの溶解における鉱物サイズ分布の変化 Mineral size distribution modeling during dissolution of montmorillonite

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In the geological disposal of radioactive waste, the waste is sealed by cement-based materials and bentonite-based material to prevent leakage into environment. The bentonite-based material protect the radioactive waste from the groundwater flow around the geological disposal area, so its low permeability should be maintained for a long term. The low permeability could be achieved by the swelling of montmorillonite in the bentonite-based material. However, montmorillonite will dissolve by a reaction with high-alkaline pore water, spoiling the low permeability of the bentonite-based material. In addition, precipitation of secondary minerals such as zeolite will promote the dissolution of montmorillonite through changes in composition of the pore water. In order to assess the long-term permeability of the bentonite-based material, it is necessary that the dissolution of montmorillonite and crystallization of secondary minerals are comprehended over a long time of several tens of thousands years.

In the pore water, there are numerous montmorillonite particles of various sizes. When montmorillonite of various sizes co-exists in the same solution, the smaller particle dissolves faster than the larger one because of the Thomson-Gibbs effect. The mean size of montmorillonite will increase gradually, leading to a delay of further dissolution. In addition, an evolution of size distribution is also important for the crystallization process of the secondary minerals, e.g., zeolite. Since zeolite is not present in the initial solution, the crystallization process is described in the nucleation and subsequent growth. Evolution of the size distribution of zeolite affects the dissolution of montmorillonite through changes in solution composition. This implies that the evolution of the size distribution of montmorillonite and zeolite should be considered to assess the long-term behavior of the permeability of the bentonite-based materials. However, in the previous chemical equilibrium calculations, the evolution of the size distribution has not been considered.

In this report, we numerically modeled the time evolution of the size distribution of montmorillonite due to dissolution according to a theoretical model described in Yao et al. (1993). The crystallization of zeolite was neglected as a first step. We consider the dissolution of montmorillonite in a closed system. The evolutions of the size distribution, bulk concentration of solution, and mean radius of montmorillonite were successfully calculated.

The model given in this report is a model in a closed system. On the other hand, the geological disposal environment is not a closed system because there is an actual mass transfer due to the flow of groundwater and diffusion. To couple the local mineral dissolution/crystallization and the global mass transfer, some chemical reaction-mass transfer calculation codes have been developed. However, these codes assumed chemical equilibrium, so the evolution of the size distribution of minerals did not considered. The evolution of the size distribution of minerals would significantly affect the long-term behavior of the permeability of the bentonite-based materials. Therefore, it is important to compare the calculation results of the model with the evolution of the size distribution and chemical equilibrium calculation result.

キーワード: モンモリロナイト, 溶解, 鉱物サイズ分布  
Keywords: montmorillonite, dissolution, Mineral size distribution

## 結晶成長実験のための画像定量解析技術の最前線 Advanced techniques in the latest quantitative image analysis for crystal growth experiments

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結晶成長実験は、ナノスケールの小さな空間から、我々が肉眼で認識できる可視的空間スケールを対象としてきた。しかし、近年では、その空間スケールはさらに拡大し、地下深部まで、あるいは軌道上の宇宙空間までを対象とするように発展した。測定の世界では、従来より xyz- t の時空間においてスケーリング則が存在するが、最先端技術の発達によってその障壁を超えることが可能となった。

干渉計やレーザ顕微鏡は試料表面を損なわずに高速データ収集が可能のため、結晶成長の長時間解析や広範囲な表面形状の観察には非常に価値の高いツールである。一定の時間間隔で取得されたデータをオフライン処理することで、時間スケールは容易に変えることができ、真の成長を追跡できる時系列データとなる。これは無人で測定された国際宇宙ステーションでのリゾチーム実験データ (Tsukamoto et al., 2013) や氷界面の観察 (Sazaki et al., 2012)、粘土の溶解速度測定 (Satoh et al., 2003) の自動処理に有効であった。

また、観察視野のシフトで得られた大量のデータ断片をオフライン処理することで、空間スケールも容易に変えることができる。一般に個別測定データにはオフセットや歪みを含み、また手作業では生成されるデータ量に補正が追いつかないため、データ全体を最終的な解析に活用できないケースが多い。そこで、市販ソフトウェアに専用の処理を行うプラグインを加えたシステムを用いて一貫した正規化や接続面の補正を行うことで測定機に起因するアーティファクトを除去することを試みた。これにより、面全体の特徴を解析するための大規模縫合が実現された。

本講演では、実際の大量データの定量解析を試みた例を紹介する。

キーワード: 画像解析, 時空間スケール, 表面形状, 大規模縫合  
Keywords: image analysis, time-space scale, topography, huge stitching

## 銀輸送体としてのIP6および銀ナノ構造の形成 IP6 as a silver carrier agent and formation of Ag nanostructures

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In recent years, people have become aware of the importance of natural organic materials in geological systems. It would be important to clarify the interaction between natural organic materials and metallic ions.

Phytic acid, known as inositol hexakisphosphate (IP6), or phytate,  $C_6H_{18}O_{24}P_6$ , is found within the hulls of nuts, seeds, and grains, and it is the principal storage form of phosphorus in many plant tissues, especially bran and seeds. IP6 is not digestible to humans and animals, and phytic acid chelates make unabsorbable certain important minerals such as zinc, iron, calcium and magnesium.

On the other hand, for many years, it has been known that silver works for its catalytic activities, anti-microbial activities, and used to avoid infections and prevent spoilage. Many researchers have focused on the anti-bacterial, ability to kill microorganisms and multi-functional properties of silver nano-particles.

In this study, it is demonstrated that IP6 plays a role as a metal carrier agent for the formation of metallic nanostructures. For the preparation of the IP6 with Ag elements (Ag-IP6), The commercial IP6 solution (50 %) was diluted with distilled  $H_2O$  at the  $H_2O:IP6$  solution ratio of 9:1, then 1g of  $AgNO_3$  was added to the diluted IP6 solution of 100 ml, and long-term stabilized small Ag clusters were formed in the solution. A drop of the solution was dripped onto metallic substrates, then kept for the treatment time of 10 s to several min at room temperature. The solution was immediately dried using a gas burner or hot plate. Then, the reaction of the Ag-IP6 with several kinds of metals was examined. The structural and morphological properties of the Ag nanostructures were characterized by scanning electron microscopy (SEM) along with energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) with EDS. In addition, the surface condition of the Ag nanostructures reacted with Cu or Al and dried IP6 complexes was characterized by X-ray photoelectron spectroscopy (XPS) using a VG, ESCA-LAB Mk II with a non-monochromatized Al K $\alpha$  source ( $h\nu = 1486.6$  eV). The energy calibration for a charge correction in the spectra was made using the C1s peak. The FTIR spectra of the dried IP6 complexes were measured using KBr disks. Each disc was composed of powders consisting of IP6:KBr~1:100. The spectra were recorded in the range of 400 to 1400  $cm^{-1}$ . Raman spectra were obtained using an NR-1800 triple Raman system with backscattering geometry using the SHG(532 nm) of a Nd:YAG laser as the excitation source. All measurements were carried out at room temperature. It was found that various kinds of Ag nanostructures were formed with additional metallic sources using the Ag-IP6. Ag nanostructures with the three-dimensional dendritic structures replaced by Cu and Mn, the two-dimensional dendritic structures replaced by  $CaSi_2$  and Mg, the two-dimensional fractal structures replaced by Fe, Ti, Al and Ni, the particles replaced by  $SrSi_2$  and the nanowires replaced by Mo and W were formed. It is noted that the IP6 plays an important role as a silver carrier agent to control the structure and morphology of the Ag nanostructures. In addition, the experimental results suggest that the structural evolution of the Ag-IP6 reacted with Cu takes place to form the Cu-IP6 complex. However, the reaction of Ag-IP6 with Al is not active.

The structural properties of the Ag nanostructures were examined, and the growth evolution of the nanostructures was discussed. The results would help us to understand the nanostructure formation by the reaction between natural organic materials and metals in nature.

Keywords: IP6, nanostructure, dendrite growth, silver

## 三次元干渉計の開発とそのタンパク質結晶成長への応用 Development and application of 3-D interferometer for analysis of the concentration field in protein crystal growth

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When the crystal is growing in a supersaturating solution, the solute concentration is decreasing towards the crystal/ solution interface because the crystal consumes solute in the solution as it grows. Due to this large vertical concentration gradient, buoyancy driven solutal convection develops. As a result, the distribution of concentration around the crystal become complicated compared to the case when there is no convection.

Thus, not only concentration gradient but also the flow and convection of the solution influences the state of the crystal surface. So that visualizing the whole concentration field of a crystal interface including convection is required.

There have been many reports concerning the measurement of the concentration field, but many of them were two-dimensional (2-D) observations, namely, the objects were observed only from one direction. The information obtained by the 2-D observations is integrated in average along the direction of the observation, so the local information, e.g., concentration distribution around the crystal-liquid interface, was not obtained.

To improve the disadvantage on the 2-D observation, a method of computer tomography (CT) has been adopted in this study. By using the CT method, we can reconstruct the information of the three-dimensional (3-D) concentration field around the growing crystal based on 2-D observations obtained from several directions (3-D observation).

In this study, 3-D measurement of the concentration field with convection and without convection around inorganic and protein crystals was carried out to reveal the concentration distribution over the crystal surfaces. Normal growth rate of the face from points to points are also measured to discuss the effect of concentration distribution on the surface.

キーワード: 干渉計, リゾチーム, 対流  
Keywords: interferometer, lysozyme, convection

## ステップ形状と成長速度から見た正方晶リゾチーム結晶の不純物吸着 Dependence of impurity adsorption on the step morphologies and growth rate of tetragonal lysozyme crystal

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High quality protein crystals are required to get the information of the 3-dimensional structure of protein molecules. Impurities, mainly dimer molecules, affect the quality of protein crystal strongly (Yoshizaki et al., 2006). In addition, it is known that the step morphology on {110} faces of the tetragonal lysozyme crystal is changed by impurities. Until now, a lot of space experiments were carried out to get high quality protein crystals under microgravity conditions (McPherson, 1993, etc.). However, the relevance between impurity effects and microgravity condition is not clear. In addition, the step morphology corresponding to the crystal external form is not observed in preceding studies.

We performed "in situ" observations under terrestrial environment and space environment using a tetragonal lysozyme crystal as the model protein. The purpose of this paper is to reveal "the influence of microgravity condition to the impurities adsorption on the {110} faces" and "the reason why the step morphology corresponding to crystal external form does not appear". We made it possible to observe the step morphology and to measure the face growth rate at the same time by using a Michelson type interferometer.

As a result of growth rate measurement, the face growth rate under microgravity condition was higher than that under terrestrial condition. An impurity works to suppress the growth rate of a crystal. Because the buoyancy-driven convection was suppressed under the microgravity condition, we assumed that the larger impurity-depletion-zone was formed around a crystal.

As a result of the observation of the step morphology, we succeeded in observing the lozenge shape step which was corresponding to an external form by a space experiment for the first time. In addition, the step morphologies were classified in four types. It is considered that the impurity adsorption on the crystal surface is different depending on the crystal orientation of the step.