

Crystal growth in magmas and zoning profiles in crystals

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There are countless documents describing various types of chemical zoning in crystals of groundmass minerals to phenocrysts in igneous rocks including plutonic to volcanic rocks. However, the origins of such zoning patterns have been still controversial to lead the quite different interpretations of formation processes of rock textures. In this talk, after briefly reviewing theoretical works of crystal growth in terms of chemical zoning in crystals, I argue the significant influence of rate law of crystal growth on the zoning profile and discuss that the growth rate is controlled by the interplay with nucleation process through the mass conservation.

The relationship between crystal growth and zoning profile was studied theoretical first by Tiller et al (1953) in metallurgy, who derived the zoning profile under the steady state condition with constant growth rates. Smith et al (1995) derived the analytical solution for time-dependent problem with constant growth rates. Lasaga (1982) obtained the representative expressions for the solution to more general cases with time-dependent growth rate as function of composition at the interface, suggesting that the oscillatory zoning cannot be formed in a binary system such as plagioclase (anorthite and albite). On the basis of his numerical model, L'Heureux (1993) argued that the effective partitioning coefficient between melt and crystal controls the occurrence of oscillatory zoning in a binary system. Recently, Gorokhova et al (2013) suggested that the multicomponent inter-diffusions play an important role in the development of oscillatory zoning as well as natural zoning pattern observed in eruption products. In these previous works, the coupling between the crystal growth and nucleation processes has not been taken into account. In the disequilibrium crystallization such as natural magmatic crystallization during volcanic eruptions, the nucleation process controls the supersaturation for crystal growth which, in turn, results in characteristic zoning profile through the mass conservation of crystallizing components and rate law of crystal growth. For instance, if we assume the constant nucleation rate, then the growth rate is found to be inversely proportional to time owing to the scaling arguments. Calculated zoning profiles well account for the observed zoning profile and core compositions as function of size for plagioclase microlites formed by the decompression-induced crystallization during explosive volcanic eruptions. Finally, I suggest that experimental reproductions of zoning profiles in systems effectively involving the nucleation process help our understanding for the natural crystallization processes especially in highly disequilibrium systems.

Keywords: crystal growth , zoning profile, nucleation

Multistep Nucleation from Vapor-to-Solid in Molecular Dynamics Simulations

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It is often observed that droplets formed from vapor are supercooled liquids in nature and experiments, although crystallization is expected to occur at temperature below the triple temperature. This phenomenon is known as an example of Ostwald's step rule in which a metastable phase appears first before a stable phase. We performed MD simulations of homogeneous vapor-to-solid phase transition of Lennard-Jones molecules, which shows multistep nucleations of formation of liquid-like particles (first step nucleation) and crystallization in those (second step nucleation). During a long direct NVE (constant number of molecules, volume and energy) integration up to 200 million steps ($= 4.3 \mu s$), the nuclei of supercooled liquid appear and growth. Crystal structure is identified using the Common Neighbor Analysis (CNA) method implemented in LAMMPS. The crystallizations of many large supercooled nano-clusters are observed after the liquid particles growth to a size (800 molecules at 60K). Some of them crystallize quickly and almost completely. We found all crystallized clusters lose a few % of their mass at freezing and every mass loss of this kind is associated with crystallization. The mass loss is caused by evaporation, since the latent heat from freezing heats up the cluster. The crystallized clusters composed of (1000-5000) atoms show various structures in our simulations. The crystallized clusters have characteristic structures for nano-particles, i.e., isosahedral (Ih), decahedral (Dh), face-centered cubic (fcc), and hexagonal close-packed (hcp). These several kinds of clusters are present in the same size range. In the simulations, once a liquid-like particle freezes, the crystal structure was kept during the growth of the crystal with the size up to 5000 molecules. Our results imply that the solid-solid transition does not occurs easily because of the energy barrier between different structures.

Keywords: crystallization, molecular dynamics simulation, nucleation

Dynamical study of initial stage of lysozyme protein crystallization by liquid-cell transmission electron microscopy

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Crystallization from solution has a key to understand geochemical processes of the earth and to synthesize functional materials. The primary stage of crystallization, called nucleation, has an important role to generate a new phase in an ambient phase. The following process is called crystal growth, which a formed crystalline nuclei grow continuously. To understand these processes in molecular scale, one of the powerful methods is direct observation of their dynamics in real-time by various microscopies. Crystal growth is well examined by in-situ observation using various advanced optical and scanning microscopies. On the other hand, nucleation process have been studied by indirect methods such as dynamic light scattering and spectroscopic methods, because nucleation process occurs at nano-scale and finishes within a few seconds and, therefore, nucleation is difficult to visualize by microscopy.. These indirect measurements suggest that nucleation is more complex process, for example, prenucleation clusters and dense liquids are formed before crystals appear. These primary particles may have critical role for nucleation of crystals, however, direct evidence is still poor because of difficulties to observe it. Recent advancement of nano-fabricate technique provides us the cells to observe liquids by transmission electron microscopy (TEM). This technique give us a chance to unveil the complex process of nucleation of minerals in nano-scale spatial resolution and real time. Here we adopt this technique to observe the nucleation process of protein lysozyme crystals. The dynamics of protein crystallization is relatively slower than that of inorganics due to their large molecular weight.

Optimizing the crystallization condition of lysozyme for TEM observation, we succeeded in observing three phases of lysozyme, amorphous and two crystalline phases. In addition, we caught the moments of nucleation of orthorhombic crystal which is the most stable phase in our crystallization condition. We measured the size evolution of nucleated particles with time, and found that the growth rate of the particle immediately after nucleation is surprisingly rapid, several hundred nm s^{-1} , which is two-three orders of magnitude faster than that of bulk lysozyme crystals. After this, growth rate is suddenly decreased, and facet faces appeared. Within several seconds from the particle appeared, growth rate became several nm s^{-1} which is the same as that of the bulk crystal at same supersaturation. Direct analysis of the nucleated particle suggests that the initial state of the nucleated particle is non-crystalline phase, and it transforms into the crystalline phase.

Keywords: In situ observation, Transmission electron microscopy, Nucleation, Crystallization, Protein crystal

2D imaging of pH change around calcium carbonate crystals during dissolution

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To understand the growth and dissolution mechanism of minerals, the pH monitoring of a solution is a useful technique. Actually a number of the previous studies has performed the pH measurements of bulk solution during the growth. However, to clarify the detail process on the surface, regional change of pH just above the crystal surface should be monitored. In the present study, we have tried to obtain two dimensional images of pH change around CaCO_3 crystals which inorganically grows or dissolves, by using the fluorescent probe 8-hydroxypyrene-1,3,6-trisul-fonic acid (HPTS) which has been applied for the research on the biogenic calcification of foraminifers. As a result, we succeeded to visualize the two dimensional distribution of pH around dissolved CaCO_3 crystal and its change with time, where pH increases above its surface. The results obtained by this technique may provide new insights into not only inorganic growth/dissolution mechanism of CaCO_3 , but also the vital effect on the biomineralization by comparing with the results for bio-related process.

Keywords: pH, calcium carbonate, dissolution

Chiral asymmetry in NaClO₃ Chiral Crystallization Induced by Circularly Polarized Laser Trapping of Plasmonic Nanoparticles

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Chirality, the property that a certain 3D structure is not superimposable on its mirror image, is a fundamental characteristic prevailing in various natural hierarchies. Living organisms preferentially select only left-handed amino acids, despite the thermodynamic equality of mirror isomers. The significant chiral bias in living organisms is known as “homochirality”, and its origin is a great puzzle on the evolution of life. Among various hypothesizes which proposed to explain the origin of biohomochirality[1-3], the extraterrestrial scenario attributes the origin to enantioselective decomposition of chiral organic compounds on a meteorite by exposure to circularly polarized light (CPL), which asymmetrically interacts with chiral matters, emitted from a neutron star.[3] Therefore, asymmetric phenomena induced by CPL irradiation is of great interest from the viewpoint of earth science. Many previous studies on photosynthesis of chiral molecule have proven that asymmetric interaction between CPL and chiral matter, i.e. circular dichroism (CD), induces slight chiral bias in enantiomeric ratio of reaction products[4]. Chiral crystallization, in which chirality spontaneously emerges in the course of crystallization, has been received attention from the viewpoint of emergence of chirality. The exploration of physical factors that induce a significant chiral bias in chiral crystallization should provide implications for the origin of biohomochirality. However, light-based chiral bias in chiral crystallization still remains unreported. The conceivable reason is that CD is intrinsically small. Here, we provide the first demonstration of a statistically-significant chiral bias in sodium chlorate (NaClO₃) chiral crystallization induced by CPL irradiation with the help of CD enhancement by localized surface plasmon resonance (LSPR) of silver nanoparticles (AgNPs), which is caused by electronic state chiral materials coupled with the collective oscillation of free electron on the surface of metal nanoparticles.

A continuous-wave (CW) CPL green laser (wavelength is 532 nm, laser power is 940±5 mW, ellipticity is 93%) was focused onto the air-liquid interface of the undersaturated NaClO₃ solution (6 microliter) containing AgNPs by using a 60× objective lens (NA = 0.9) equipped on an inverted polarized light microscope. We repeated crystallization and chirality identification of the NaClO₃ crystal 150 times by using *l*-CPL and 150 times by using *r*-CPL, respectively. The number of the resulting enantiomorphs was counted. The crystallization dynamics was examined by *in-situ* microscopic observation of Raman scattering and polarized image.

Upon the laser irradiation, aggregates of the AgNPs occasionally floated on the air-liquid interface were trapped at the focal spot because of optical trapping. Crystallization was induced simultaneously with the optical trapping of AgNPs. The observation of Raman scattering showed that crystallization occurred at the moment when surface-enhanced Raman scattering (SERS) [5] active particle was optically trapped, showing that the excitation of LSPR plays significant role for nucleation [6]. As the result of counting the given enantiomorphs, the crystallization using *l*-CPL(*r*-CPL) yielded *l*-enantiomorph 55(93) times and *d*-enantiomorph 95(57) times, respectively[7]. These results indicate that the “dominant” enantiomorph can be switchable by changing the handedness of incident CPL, i.e. enantioselectivity. This chiral bias is statistically significant because the number of the “dominant” enantiomorph deviates 99% interval of

the binomial distribution $B(n,p) = B(150, 0.5)$, where n is the number of trials and p is the probability that the “dominant” enantiomorph crystallizes out. The chiral bias, which was approximately 25% in crystal enantiomeric excess, is much higher than that in typical enantiomeric excess in photosynthesis ranging from 0.5 to 2% [8].

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In-situ observations of sublimation processes of snow crystals

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We observed snow crystals using specially designed experimental systems in hand-made igloo-like snow laboratories at the base of Asahi-dake in the Taisetsu area, Hokkaido, Japan. The altitude of the observation site is approximately 1100 m. We visited the site at the end of January or beginning of February in 2015-2017 and stayed 8 nights in total. The temperature range in the snow laboratory during the observation is -6 to -11°C in general and the humidity has been naturally controlled close to 100% because all the walls of the laboratory made of snow.

Our experimental systems are composed of the environment controlled cell and the Mach-Zehnder-type laser interferometer or the Michelson-type white-light interferometer microscope with a long working distance, and the optimized color-filtered optical microscopes. The aim of the environment controlled cell is to control the growth and sublimation of the snow crystals. To control the temperature inside the environment controlled cell, the cell has been sandwiched by two Peltier devices (26 mmf × 3.7 mm) attached with a copper plate with an opening (10 mmf) at the center for optical observations. The opening is covered by a glass plate. To control the vapor pressure of water inside the cell, an evaporation source of water vapor has been prepared at the bottom of the cell. The temperature of the water source is measured by a chromel-alumel thermocouple. A snow crystal is stuck on the tip of a glass rod smaller than 1 mm in diameter and inserted into the cell from the roof of the cell. Temperature near the snow crystal is measured by a platinum resistance temperature detector.

We collected snow crystals directly on a black felt just outside the snow laboratory and selected a snow crystal, which was put onto a glass plate for general observations of the shape and surface textures or onto the tip of the glass rod to observe sublimation and growth rates in the controlled environment. In this presentation, we will report our attempts of in-situ observation and results including sublimation rates of the snow crystal observed using our experimental systems.

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Keywords: Snow, In-situ observation, Interferometry, Optical microscope

Crystallographically Favored Attachment of Just-Nucleated MoO₃ Nanoparticles in Gas Current

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Nucleation and subsequent growth processes via homogeneous nucleation in vapor are enigmatic. To investigate evolution of phases, chemical composition and shape of just-nucleated nanoparticles in cooling evaporant, we developed a noble experimental apparatus that enables in-situ spatial scan of nucleating and growing nanoparticles with transmittance FT-IR spectroscopy. Here we experimentally show direct evidence that molybdenum oxide nanoparticle, just-nucleated from evaporated vapor, grown via attachment with crystallographically favored orientation in a gas current generated by the evaporation source. Just-nucleated nanoparticles showed characteristic IR absorbance of needle shaped MoO₃ and gradually changed into that of cubic and polyhedral shaped MoO₃ in ascending gas current. Each IR feature is consistent with that obtained by ex-situ IR measurements and morphological evolutions of collected nanoparticles. All needle, cubic and polyhedral shaped nanoparticles are attributed to MoO₃ with monoclinic crystal structure. The needle shaped nanoparticles are always elongated to [100] direction. Some particles, collected at growing zone, were partially attached at perpendicular planes to (100). We consider that the needle shape is the result of anisotropic growth of just-nucleated nanoparticles in supersaturated vapor. Then, the attachment between needle shaped particles fortuitously collided with the favorable orientation resulted in formation of cubic and polyhedral shaped particles in a gas current. These findings enrich the view on the pathways in nucleation and growth in vapor and give new insights into inter-particle forces that drive oriented attachment growth.

Keywords: Homogeneous Nucleation, Oriented Attachment

In-situ observation of Liquid Layers on Ice Crystal Surfaces Induced by Hydrogen Chloride Gas

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Surface melting of ice crystals forms quasi-liquid layers (QLLs) on ice surfaces, and affects a wide variety of natural phenomena. Since QLLs enhance various chemical reactions in ice clouds, the formation of QLLs by atmospheric gases has been studied intensively. However, such studies were performed using spectroscopy techniques, which have low spatial resolution. Here we show the first direct visualization of QLLs on ice basal faces in the presence of hydrogen chloride (HCl) gas (model atmospheric gas) by advanced optical microscopy, which can visualize individual 0.37-nm-thick elementary steps [1] and QLLs [2] on ice crystal surfaces. We found that the HCl gas induced the appearances of QLLs with a droplet shape in the temperature range of -15.0 ~ -1.5°C, where no QLL appears in the absence of HCl gas [3]. This result indicates that HCl gas adsorbed on ice crystal surfaces probably changed the surface structure of ice crystals and then induced the subsequent melting of ice surfaces. We also observed the movement, shape change, and splitting of the droplet QLLs when water vapor was undersaturated. The long-term (one-hour) existence of the droplet QLLs under the undersaturated conditions strongly suggests that the droplet QLLs were thermodynamically-stable HCl solutions. In addition, we found that the HCl induced droplets were embedded into ice crystals by growth of ice crystals and the embedded droplets appeared again by evaporation of ice crystals. These results show the possibility that ice crystals can store large amount of gas components as fluid inclusions.

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Keywords: Ice, Surface melting, Quasi-liquid layer, Hydrogen chloride gas, Advanced optical microscopy

Numerical study on crystal growth hysteresis in spiral growth

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Step dynamics is one of the fundamental physical processes of crystal growth. There are numerous steps with atomistic-scale heights on the crystal surface. A growth unit such as an atom or molecule that lands on the surface usually migrates laterally until it reaches the steps –or until it desorbs into the mother phase. The growth unit that reaches a step becomes incorporated into the crystal, leading to advancement of the step. Every passage of the step increases the height of the surface by a monolayer (layer-by-layer growth). Therefore, the understanding of what determines the generation of steps and the rate of the advancement is essential to elucidate the crystal growth mechanism. In this study, we focus attention on the growth hysteresis, which is one of the impurity-induced phenomena on the step dynamics.

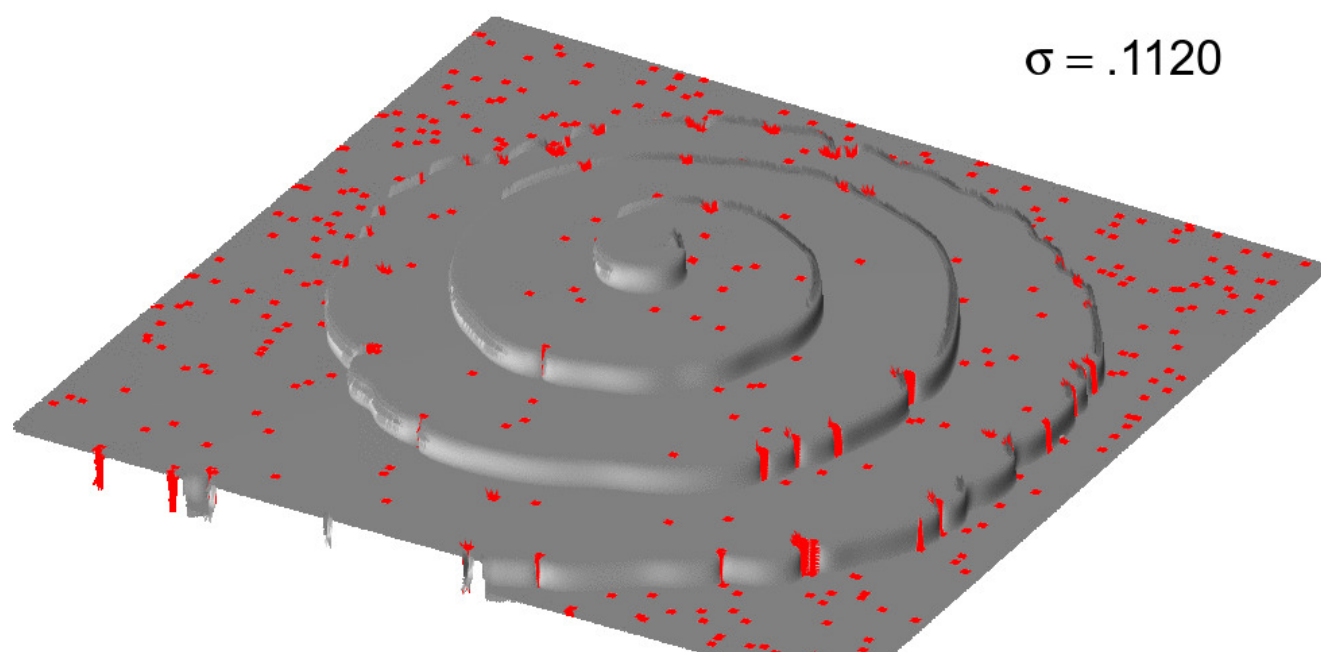
Let us consider the crystal growth from aqueous solution. When the solution includes impurities, the crystal growth rate when the supersaturation is increased is different from that when it is decreased. The growth hysteresis has been observed in some experimental setups with different combinations of crystal and impurity, suggesting the existence of some universal impurity effect. Therefore, the elucidation of the growth hysteresis mechanism leads to deepen our knowledge of impurity effects on crystal growth. It has been considered that the hysteresis results from the interaction between the impurities adsorbed on the crystal surface and advancing steps. As the supersaturation is decreased, the step velocity is decreased, leading to the increase in ad-impurities, then it retards the step advancement further. This positive feedback causes the catastrophic change in the step velocity. Once the step motion stops, the surface will be polluted by ad-impurities until the impurity desorption and adsorption reach equilibrium. Therefore, it is difficult for the step to restart again even if the supersaturation is increased again; namely, it is hysteresis. The interdependence between the step velocity and the number of ad-impurities was formulated based on a mean field approximation, elucidating the existence of multi-solutions of the step velocity at a certain supersaturation region [1]. In addition, the numerical simulations reproduced the hysteresis of the step velocity in the realistic situation on which the mean field approximation is inapplicable [2]. In this study, we investigate the hysteresis of the growth rate normal to the crystal surface.

We adopt a numerical scheme that combines a phase-field (PF) method and a Monte Carlo (MC) method [2]. In this scheme, the step dynamics is solved by the PF method and the random impurity adsorption-desorption kinetics is modeled by the MC method. We introduce a screw dislocation on the crystal surface as a step source. We start the calculation from an impurity-free surface and repeat down-and-up cycles of supersaturation. When the supersaturation is decreased, the normal growth rate drops at a certain supersaturation. When the supersaturation is increased, the normal growth rate increases rapidly to that in the impurity-free case. The catastrophic changes appear in every cycle. The supersaturation at which the normal growth rate drops is different from that when it is increased; namely, the hysteresis is reproduced. The hysteresis appears in the supersaturation range as predicted by the mean field theory.

To summarize, we prove that the hysteresis of the normal growth rate is caused by the same mechanism with that of the step velocity. The supersaturation range at which the hysteresis appears can be derived from physical quantities relating to the step advancement and impurity adsorption-desorption kinetics, so we might be able to evaluate these quantities by comparison with experiments.

Reference: [1] H. Miura and K. Tsukamoto, 2013, Cryst. Growth Des. 13, 3588-3595. [2] H. Miura, 2016, Cryst. Growth Des. 16, 2033-2039.

Keywords: Crystal growth, Hysteresis, Spiral growth, Numerical simulation



Direct TEM observation of pozzolanic reaction of silica fume in $\text{Ca}(\text{OH})_2$ solution

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Glassy materials, such as fly-ash, silica fume and volcanic ashes are industrially used as resource materials of concrete aggregates, applied for cement-solidification technique. As a concept, advantage of utilization of these materials is based on their relatively higher solubility than crystalline materials. Until recently, there are numerous studies to optimize the solidification condition with cementitious materials involving alkalis and water. Currently, a number of concretion methods was proposed and still developed for construction. More recently, classical cement-based method is evolving to geopolymer technique, but the early reaction of concretion is essentially common because the dissolution is always prior to precipitation. In order to precise and optimize the concretion condition, we carried out direct observation of concretion using TEM equipped with newly developed cell (Protochips, Poseidon, e.g., Yamazaki et al., 2017) which is specialized for liquid-bearing samples. System comprised of silica fume, H_2O and $\text{Ca}(\text{OH})_2$ solution at room temperature was investigated in nanometer scale.

As the result, silica hydration can be detected semi-quantitatively from TEM images. Silica spheres in H_2O are expanded and reduce their integrated contrasts, suggesting simultaneous hydration and dissolution. The expansion was monitored for observation periods over 4000 s to be in the velocity of $9.2\text{E-}3$ and $3.7\text{E-}3$ nm/s at zero and 1.0 $\mu\text{l/min}$ flow, respectively. Their dissolution rates were measured to be $6.5\text{E-}5$ and $2.0\text{E-}4$ mol/m²/s, respectively. When we switched the solution from H_2O to $\text{Ca}(\text{OH})_2$ (equilibrated at 25 degC), the silica spheres start fast expansion again in the velocity of $2.6\text{E-}2$ nm/s, but dissolution rates were extensively reduced over the measurement period of 2400 s. During these expansion processes in $\text{Ca}(\text{OH})_2$ solution, silica spheres were not only expanded but also accompanied with precipitation of film to veil-shaped CSH (calcium silicate hydrate) phase which is surrounding the spheres. During propagation of this CSH phase in the velocity of 5.3 nm/s, the spheres were getting porous and losing its original density explained such by so-called “shrinking core” model. This should be interpreted as the true process of so-called “pozzolanic” reaction. Parallel to the in-situ observation, we reproduced the observation with ex-situ method on a batch reaction system held for 3000 min. It clearly exhibited that spheres after 60 min started 2-D nucleation of unknown phase, then filmy to veil-shaped phase successively developed and enclosed the original spheres together. Elemental analyses with FESEM-EDS represented that the Ca/Si ratios of these secondary phases increased from 0.1 to 0.2 with curing periods (20 to 72 h), probably due to the systematic dissolution/precipitation balance. This can be interpreted as the essential process of cement solidification. Thus, colloidal glassy material can be aggregated and evolved to be self-consolidation state in alkaline solution. Classical knowledge of pozzolanic reaction can provide us an important information about controlling and evolving the colloids to hard materials.

Keywords: direct TEM observation, pozzolanic reaction, silica fume

Specific surface free energy of graphite crystals

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In order to discuss crystal growth, specific free energy (SSFE) is significant value and theoretically well studied. However, the determination of SSFE of solid is difficult. We calculated SSFE of many crystal using contact angle of liquids and discussed the relationships with crystal growth.

Highly oriented pyrolytic graphite(HOPG), grafoil and natural graphite were used as crystal samples. Contact angles of water and formamid were observed using sessile drop method. Crystal faces of HOPG can be classified to edge and plane faces. Contact angle of water on the plane face of HOPG was 79.7 degree, and that of formamid was 68.1 degree. The contact angle of water and formamid on the edge face of HOPG was 59.2 and 52.5 degree, respectively. The contact angle of water on grafoil was observed to be 68.1 degree and that of formamid was 53.4 degree. Contact angle water on the natural graphite showed two peaks, for 76 and 102 degree, but the contact angle of formamid one peak at 53.4 degree.

SSFEs were calculated from contact angle using Wu and Fowkes approximation. Calculated SSFE for plane and edge faces of HOPG were 27.4 and 44.9 mN/m. The SSFE of grafoil was 39.1 mN/m. Two peaks of contact angle of natural graphite were calculated to be 40.6 mN/m(graphite-p), and 79.5 mN/m(graphite-e). The crystal face of natural graphite with lower SSFE was considered to correspond to plane face, and the higher SSFE corresponds to the edge face of graphite.

Keywords: Graphite, Specific surface free energy, Orientation