

マグマにおける結晶成長と結晶中の累帯構造

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.

キーワード：結晶成長、累帯構造、核形成

Keywords: crystal growth, zoning profile, nucleation

気相から固相への多段階核生成の分子動力学シミュレーション

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

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核生成過程は、理工学の幅広い分野で重要なプロセスであるが、分子レベルでの理解は未だ限られている。これまで我々は気相からの核生成過程の分子動力学 (MD) シミュレーションを行い、相変化の様子を調べてきた[1,2]。MD計算では3重点以下のさまざまな温度下で計算しても、凝縮核は液相であることを示していた。このような現象はオストワルドの段階則として考えられ、初めに生成した過冷却液滴の凝縮核は、ある段階で安定相である結晶になることが期待される。我々は最大1500万の希ガス (Lennard-Jones分子) を用い、3重点以下の温度で気相から液相への核生成および液滴からの結晶化という多段階核生成過程のMD計算を行った。粒子数、体積、エネルギー(NVE)一定の系で、凝縮核が結晶化するには長い待ち時間が必要なため、数億ステップ (実時間で数 μ s) の計算を行った。計算には並列計算用の分子動力学計算コード(LAMMPS)を用い、国内外の並列計算機(チューリッヒ大、国立天文台)を利用した。MD計算の結果、気相分子から準安定相である過冷却液滴が多数生成し、その後過冷却液滴内の一部分から核生成が始まり短時間で結晶核が広がり全体が結晶化する様子が得られた。液滴の結晶化はすぐには起きず、ある程度大きく成長してから起きること、生成されたナノ結晶は5回対称性を持つ正20面体、十面体の準結晶、面心立方格子(fcc)に富む結晶、六方最密重点構造(hcp)に富む結晶が混在していること、また結晶化する際には蒸発を伴うことなどが明らかになった。

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キーワード：結晶化、分子動力学計算、核生成

Keywords: crystallization, molecular dynamics simulation, nucleation

溶液透過型電子顕微鏡によるリゾチームタンパク質の結晶化初期過程の動力学的研究

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.

キーワード：その場観察、透過型電子顕微鏡、核生成、結晶化、タンパク質結晶

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

溶解する炭酸カルシウム近傍におけるpH変化の2次元イメージング 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.

キーワード：pH、炭酸カルシウム、溶解

Keywords: pH, calcium carbonate, dissolution

プラズモンナノ粒子の円偏光光学捕捉により誘起される塩素酸ナトリウム結晶化におけるキラリティの偏り

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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雪の結晶の昇華過程のその場観察

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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キーワード：雪、その場観察、干渉法、光学顕微鏡

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.

キーワード：均質核生成、オリエンテッドアタッチメント

Keywords: Homogeneous Nucleation, Oriented Attachment

塩化水素ガスによって氷表面に生じる液体層のその場観察

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 $-15.0 \sim -1.5^{\circ}\text{C}$, 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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キーワード：氷、表面融解、疑似液体層、塩化水素ガス、高分解能光学顕微法

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

らせん成長する結晶に現れるヒステリシスの数値計算

Numerical study on crystal growth hysteresis in spiral growth

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ステップ・ダイナミクスは、結晶成長における本質的な物理過程のひとつである。結晶表面には原子スケールの高さを持つ段差（ステップ）が存在し、そこに原子や分子が取り込まれることによってステップが前進し、結晶が一層ずつ積み上げられていく（層成長モデル）。従って、結晶成長メカニズムを解明するには、ステップの供給メカニズムやステップ前進速度を決める物理を理解する必要がある。本研究では、結晶表面に吸着した不純物と前進ステップとの相互作用によって引き起こされる「成長ヒステリシス」に着目した。

成長ヒステリシスとは、結晶化駆動力（例えば、過飽和度）を減少させたときと増加させたときとで、結晶成長速度の履歴が異なる現象である。いくつかの結晶と不純物の組み合わせに対して成長ヒステリシスが観察されていることから、そこにはなんらかの普遍的な不純物効果が作用していることが示唆される。従って、成長ヒステリシスの発生メカニズムを解明することは、結晶成長における不純物効果の理解に繋がる。成長ヒステリシスの要因としては、結晶表面に付着した不純物と前進ステップとの相互作用が検討されてきた。駆動力を減少させていくと、ステップ前進速度が低下し、それによって吸着不純物が増加し、それがさらにステップ前進速度の低下を招くというポジティブ・フィードバックによって、ステップの前進が突然停止する（カストロフィック変化）。ひとたびステップ前進が停止すると、不純物の脱離吸着が平衡に達するまで吸着不純物が増加する。そのため、次に駆動力を増加してもなかなかステップが再始動しない。すなわち、ヒステリシスが現れることになる。このステップ前進速度と吸着不純物量の相互依存関係は平均場近似に基づいて定式化され、ある過飽和度領域において異なる複数の定常解が存在することが明らかとなった[1]。また、平均場近似が成り立たない現実的な状況を想定した数値計算によって、複数定常解が存在する過飽和度領域においてステップ前進速度のヒステリシスが再現された[2]。しかし、成長ヒステリシスはステップ前進速度だけでなく、結晶の面成長速度においても観察されている。面成長速度は、ステップ前進速度だけでなく、ステップの供給機構にも依存する。そこで、本研究では、代表的な成長様式であるらせん成長を想定し、面成長速度における成長ヒステリシスについて調べた。

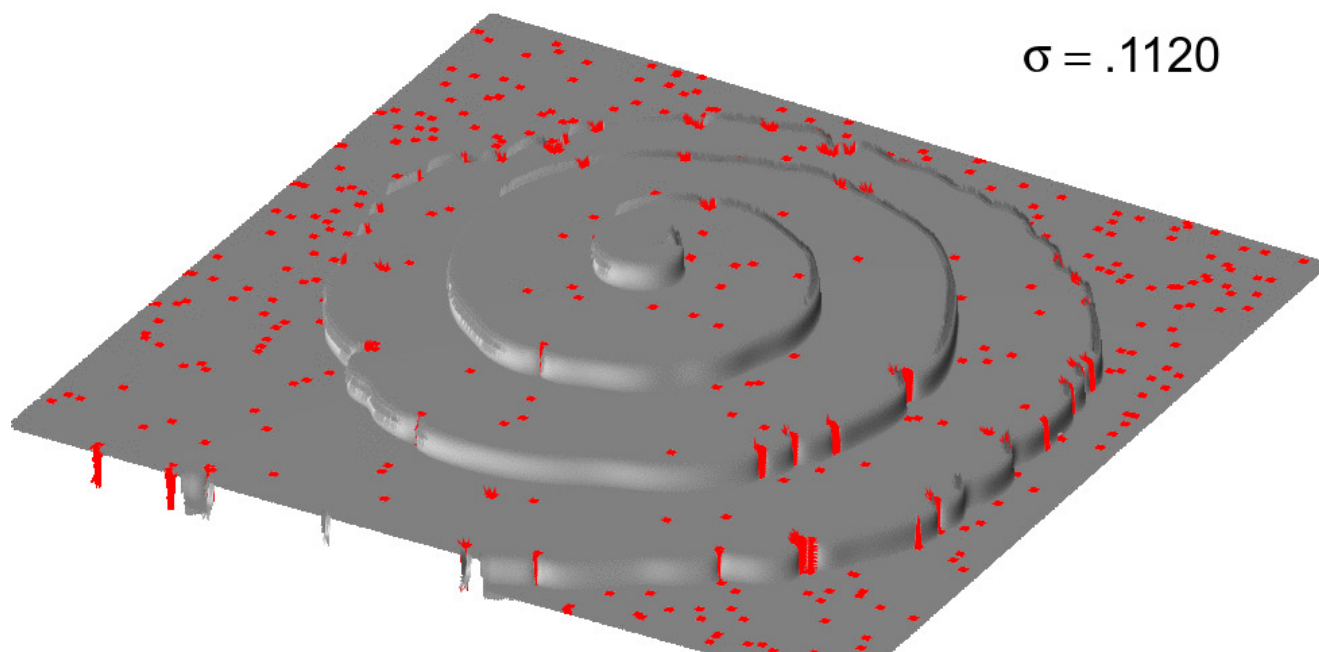
数値計算法としては、フェーズフィールド（PF）法とモンテカルロ（MC）法を組み合わせたモデル[2]を用いた。この手法では、ステップ・ダイナミクスをPF法で、結晶表面におけるランダムな不純物脱離吸着をMC法で解く。結晶面にはらせん転位をひとつ導入し、連続的にらせんステップが供給されるようにした。初期状態として、不純物がまったく吸着していない結晶表面を用意し、結晶の成長と不純物の脱離吸着を開始させた。時間とともに過飽和度を一定率で減少させ、その後、増加させるというサイクルを繰り返し、面成長速度の履歴を調べた。過飽和度を減少させたとき、面成長速度はある過飽和度において急激に減少し、ほぼゼロとなった。その後過飽和度を増加させたとき、面成長速度はある過飽和度において急激に増加し、不純物がないときと同程度まで回復した。この過飽和度のわずかな変化による面成長速度の急激な変化（カストロフィック変化）は、いずれのサイクルにおいても確認された。面成長速度が急激に減少するときの過飽和度は、急激に増加するときの過飽和度とは明らかに異なっており、ヒステリシスが再現された。面成長速度の急激な変化が生じる過飽和度は、平均場理論の予言とほぼ一致した。

以上の結果より、結晶の面成長速度に見られるヒステリシスも、ステップ前進速度と同様のメカニズムで生じることが明らかとなった。すなわち、結晶表面における不純物の「遅い」脱離吸着、及び、吸着不純物による前進ステップのピンギング効果である。ヒステリシスが現れる過飽和度の値やその範囲は、ステップ前進や不純物脱離吸着に関する物理量から算出できるため、実験データと比較することで種々の物理量の推定が可能になると期待される。また、ステップ・ダイナミクスにおける不純物効果の理解も進展するであろう。

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

キーワード : 結晶成長、ヒステリシス、らせん成長、数値計算

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



Direct TEM observation of pozzolanic reaction of silica fume in Ca(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, H₂O and Ca(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 H₂O 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 9.2E-3 and 3.7E-3 nm/s at zero and 1.0 ul/min flow, respectively. Their dissolution rates were measured to be 6.5E-5 and 2.0E-4 mol/m²/s, respectively. When we switched the solution from H₂O to Ca(OH)₂ (equilibrated at 25 degC), the silica spheres start fast expansion again in the velocity of 2.6E-2 nm/s, but dissolution rates were extensively reduced over the measurement period of 2400 s. During these expansion processes in Ca(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.

キーワード：直接TEM観察、ポゾラン反応、シリカヒューム

Keywords: direct TEM observation, pozzolanic reaction, silica fume

黒鉛結晶における表面自由エネルギー密度の評価

Specific surface free energy of graphite crystals

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緒言

結晶成長を論じるために結晶の表面自由エネルギーについては多くの理論的研究が行われてきた。しかし実験的に固体の表面自由エネルギーを測定するのは不可能と言われ、結晶の表面自由エネルギーを実測した例は非常に少ない。我々はこれまで液体の接触角からさまざまな結晶の表面自由エネルギーを算出し、結晶成長との関係を論じてきた。今回は単一の元素からなるグラファイトに注目し表面自由エネルギー密度と結晶子の配向との関係を議論する。

実験

HOPG, Grafoil. 天然のグラファイトの3種類をグラファイト試料として用いた。

HOPGにおいては、結晶子のplane部とedge部に分けて測定した。

接触角は2液法により測定した。水とホルムアミドの2種類の液滴を使用し、それぞれ0.1 μl ずつマイクロピペットでサンプル上に滴下した。滴下した液滴をデジタルカメラにより撮影し、パソコン上で接触角の測定を行った。

結果

各サンプルの接触角を測定し、平均接触角を算出した。HOPGではplane部で水79.7°ホルムアミド68.1°、edge部で水52.5°ホルムアミド59.2°となった。Grafoilでは水68.1°ホルムアミド53.4°となった。天然のグラファイトではホルムアミドは53.4°となった。しかし、水では、76°と102°という2つの接触角が測定されたため、それぞれ小さいほうをwater1、大きいほうをwater2とした。

考察

測定された接触角を用い、Wuの調和平均式及びFowkes近似式より各サンプルの表面自由エネルギー密度を算出した。HOPGでは、plane部が27.4mN/m, edge部が44.9mN/mとなった。また、Grafoilは、39.1mN/mとなった。一方、天然のグラファイトは2つの接触角より40.6mN/mと79.5mN/mの2種類の表面自由エネルギーが算出された。それぞれplane部とedge部に相当すると考えられるため、それぞれgraphite(plane), graphite(edge)とした。HOPGのplane部とedge部を比べるとedge部のほうが

SSFEの値が大きくなっていることがわかる。それはplane部よりedge部のほうが化学的に不安定なためと考えられる。またHOPG(plane), Grafoil, Graphite(plane)の順にSSFEの値が大きくなっているのはHOPGではステップの少ないのに対して、grafoilではステップの多い面が、graphite(plane)ではステップやキンクが多い面がそれぞれ出ているためと考えられる。

キーワード：黒鉛、表面自由エネルギー密度、配向性

Keywords: Graphite, Specific surface free energy, Orientation