In-situ observations of sublimation processes of snow crystals

*Yuki Kimura[1], Tomoya Yamazaki[1], Takao Maki, Yoshinori Furukawa[1]

1. Institute of Low Temperature Science, Hokkaido University

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 MoO_3 Nanoparticles in Gas Current

*Shinnosuke Ishizuka[1], Yuki Kimura[1], Rikako Satoh[1], Tomoya Yamazaki[1], Tetsuya Hama[1]

1. Institute of Low Temperature Science Hokkaido University

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 MoO_3 and gradually changed into that of cubic and polyhedral shaped MoO_3 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 MoO_3 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

*Ken Nagashima[1], Gen Sazaki[1], Tetsuya Hama[1], Ken-ichiro Murata[1], Yoshinori Furukawa[1]

1. The Institute of Low Temperature Science, Hokkaido University

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 evapolation of ice crystals. These results shows the possibility that ice crystals can store large amount of gas components as fluid inclusions.

[1] Sazaki et al. (2010) PNAS 107, 19702.
[2] Sazaki et al. (2012) PNAS 109, 1052.
[3] Nagashima et al. (2016) Cryst. Growth Des. 16, 2225.

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

Numerical study on crystal growth hysteresis in spiral growth

*Hitoshi Miura[1]

1. Graduate School of Natural Sciences, Department of Information and Basic Science, Nagoya City University

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.

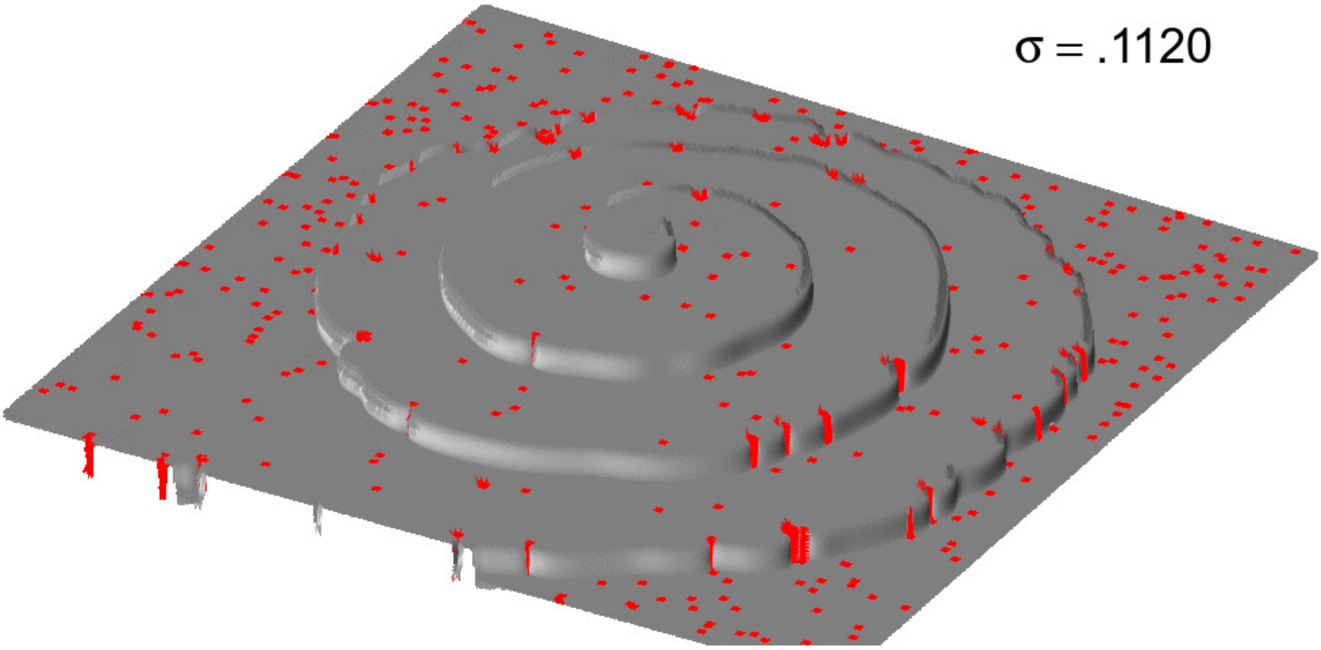
Let us consider the crystal growth from aqueous solution. When the solution includes impurities, the crystal growth rate when the supersaturation is increased is different from that when it is decreased. The growth hysteresis has been observed in some experimental setups with different combinations of 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 $Ca(OH)_2$ solution

*Hisao Satoh[1], Yuki Kimura[2], Tomoya Yamazaki[2], Erika Furukawa[3]

1. Naka Energy Research Laboratory, Mitsubishi Materials Corporation, 2. Institute of Low Temperature Science, Hokkaido University, 3. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University

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 $Ca(OH)_2$ 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 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 9.2E-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/m^2/s, respectively. When we switched the solution from H_2O 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.

Keywords: direct TEM observation, pozzolanic reaction, silica fume

Specific surface free energy of graphite crystals

*Yoshimura Takumi[1], Kohei Saito[1], Takaomi Suzuki[1]

1. Shinshu university

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 peeks, for 76 and 102 degree, but the contact angle of formamid one peek at 53.4 degree.

SSFEs were calculated from contact angle using Wu and Fowkes approximation. Calculated SSFE for plane anf edge faces of HOPG were 27.4 and 44.9 mN/m. The SSFE of grafoil was 39.1 mN/m. Two peeks 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