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Nanoscopic characteristics of anhydrite (100) surface growth under mild hydrothermal conditions

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Anhydrite ($CaSO_4$) is a major component of evaporitic rocks and is currently forming in submarine hydrothermal fields, where its dissolution and precipitation plays a significant role in controlling porosity. Anhydrite also is a component of undesirable scale on heat transfer surfaces during desalinization and waste water treatments. Knowledge of the molecular processes that control anhydrite growth and dissolution is crucial to understand the geochemical cycling of elements in some natural systems and to develop strategies to limit scale formation on hot surfaces in numerous industrial processes.

Several works investigated the nanoscale characteristics of anhydrite growth and dissolution at 25ºC [1,2]. However, primary anhydrite mainly forms at temperatures above 60ºC. In this work we study the growth of anhydrite (100) surface in contact with supersaturated aqueous solutions ($\beta_{\text{anhydrite}}$ = 1-3.6) under mild hydrothermal conditions (T = 50-115ºC, P = 1 atm). The experiments were performed using a hydrothermal atomic force microscope (HAFM) [3]. Our observations showed that: (i) anhydrite (100) surface grows by lateral spreading of monomolecular layers (3.5 Å in height), which originate at cleavage steps, (ii) the growth is highly anisotropic, with very significant differences in advance speed along different directions ($S_{[001]}$ (or $S_{[00\text{-}1]}$) >> $S_{[011]}$ > $S_{[010]}$), (iii) growth anisotropy is especially evident for <001>, with [001] and [00-1] alternating as fast and slow directions in successive monolayers, (iv) these growth characteristics determine that fast-moving steps combine with slow-moving steps to form bilayer steps around screw dislocations, (v) a reduced number of two-dimensional nuclei (≤ 1nuclei/µm^2) forms at T ≥ 80ºC and $\beta_{\text{anhydrite}}$ ≥ 2, (vi) two-dimensional nuclei also are monomolecular and their pseudo-triangular shape also reflects the growth anisotropy.

Most of anhydrite (100) surface growth characteristics at mild hydrothermal conditions coincide with those reported for its growth at 25ºC [2], which evidences that the strong structural control observed at room temperature extends into higher temperature conditions. The marked growth anisotropy results from the non-equivalent geometry of [010] and [0-10] steps in the monolayer. The existence of two-fold screw axes along [100] explains the alternation of [001] and [00-1] as fast-moving and slow-moving directions in successive monolayers. Highly anisotropic growth at the nanoscale seems to be a feature common to crystal surfaces perpendicular to two-fold screw axes.

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Double wavelength interferometry for direct observation of homogeneous nucleation in vapor phase

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To investigate the homogeneous nucleation and growth process of nanoparticles in vapor phase, interferometric observation using two lasers with different wavelengths was attempted for the fist time to the gas evaporation method, which has been a commonly accepted physical production method of nanoparticles. Using the gas evaporation method, fine particles with the size of several nm to ~100 nm are directly produced from the gas phase. When an evaporant is initiated in an inert gas, the evaporated vapor subsequently cools and condenses in the gas atmosphere, i.e., nanoparticles are obtained via homogeneous nucleation from the vapor phase. In this manner, nucleation will occur far from the equilibrium state, but it is not obvious how far condensation takes place. Although there are reports concerning homogeneous and heterogeneous nucleation from solution phases [1], there are very limited reports concerning homogeneous nucleation from a vapor phase in recent years. Homogeneous nucleation rates of droplets were measured as a function of temperature and supersaturation using ethanol and nonane [2], [3]. The nucleation rates were different in several orders of magnitude from the classical nucleation theory. There is also no report concerning nucleation and few studies in view of crystal growth for smoke experiment, although significant numbers of smoke experiments have been performed so far.

We constructed a new smoke generator and applied two lasers with different wavelengths at 532 and 632.8 nm for a Mach-Zehnder type interferometer. By the use of double laser, two unknown parameters can be obtained simultaneously, i.e., concentration of evaporated vapor and ambient temperature. As the result, not only condensation temperature but also supersaturation, growth rate and sticking probability are measurable.

In preliminary experiment using single laser at 632.8 nm, tungsten oxide was evaporated by electrical heating of a tungsten wire in a mixture gas of Ar and O_2. WO_3 nanoparticles were formed via homogeneous nucleation and growth during a gas cools following a thermal convection produced by the evaporation source. The degree of supersaturation for nucleation was extremely high, 6.6×10^6, which was determined from the interferogram. Surface free energy of WO_3 at 1100 K was calculated based on the classical nucleation theory and was 1.38×10^3 erg cm^{-2}, which is within the reported values. Homogeneously condensed WO_3 nuclei initially maintain their temperature for ~5 ms and then cool down with a rate of ~5×10^4 K/s. A part of the difference between actual formation rates of produced nanoparticles, which were determined based on a transmission electron microscope, and theoretical values were well explained if we adopt the idea of coalescence growth.

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