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結晶成長速度の振動現象とヒステリシスにおける不純物の役割
Role of impurity on oscillatory growth and growth hysteresis of crystals

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Crystals characterized by oscillatory zoning show a quasi-cyclic alternation in the chemical composition in the growth direction, from a few tens of nanometers to several tens of micrometers in thickness. Such mineral zoning is a common phenomenon in magmatic rocks, hydrothermally altered rocks, mineralized rocks, and carbonate sequences. Oscillatory zoning may originate from external fluctuation or an intrinsic mechanism. In the first case, oscillatory zoning is induced by periodic changes in external growth conditions such as temperature, pressure, and solution composition. In the second case, the complex diffusion-attachment processes at the solution-crystal interface is considered to result in oscillatory zoning even under stable growth conditions. Some experimental studies have reproduced oscillatory zoning in the absence of external fluctuation, suggesting that the intrinsic mechanism plays an important role in some crystallization systems.

An important factor that affects the crystal growth kinetics is impurity, which is known to inhibit crystal growth. Pinning is a well-known effect of impurities on the kinetics of crystal growth in solution. Step advancement is pinned (or stopped) by impurities at the points of adsorption on the crystal surface. The step is forced to curve; the advancement velocity of the curved step is reduced by the Gibbs-Thomson effect. The time-averaged step velocity decreases with an increase in the density of adsorbed impurities and a decrease in supersaturation at the crystal surface. The pinning mechanism has been discussed successfully for various crystallizing systems with different impurities. It also accounts for the growth hysteresis, namely, two different growth velocities are observed at a given supersaturation, depending on the change in supersaturation (decrease or increase). However, the role of impurities on oscillatory growth has not been modeled on a physical basis to date.

We consider the adsorption and desorption of the impurities on the growing crystal surface along with the pinning mechanism. If the steps barely pass beyond a certain area on the crystal surface, the adsorption and desorption of impurities reach an equilibrium state (Langmuir isotherm). In contrast, repeated passage of steps shortens the exposure time of adsorption sites for impurities, and this tends to decrease the density of the adsorbed impurities. Frequent step passages will result in less impurities at the surface, as if the crystal surface is swept by the advancing steps. Because of impurity sweeping coupled with pinning, there is a potential feedback on the change in the step velocity through the change in the impurity density. The feedback loop causes periodic oscillation of the step velocity.

We propose a new mechanism of oscillatory growth and growth hysteresis based on step pinning by impurities adsorbed on the growing crystal surface. This model is very simple and is based on physically clear assumptions. The range of supersaturation over which the growth hysteresis appears is given by denite physical parameters such as step free energy, number density of the adsorbed impurities, and timescale of impurity adsorption. This mechanism is robust in the crystallization system from solution with existence of impurities.

キーワード: 結晶成長, 振動現象, ヒステリシス, ピニング機構, 不純物
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