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Numerical simulations of flow and mass transfer during potassium dihydrogen phosphate single crystal growth via the three-dimensional motion growth method

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ABSTRACT

A novel solution-based crystal growth method, namely, the three-dimensional motion growth method (3D MGM) is proposed to effectively utilize convection for simultaneous enhancement of morphological stability and mass transfer. To evaluate this new growth method, numerical simulations of flow and mass transfer are carried out on growth of potassium dihydrogen phosphate (KDP) crystals subjected to 3D MGM. The supersaturation field of the crystal surface is presented as functions of translational velocity and distance since it is critically involved in the processes of morphological instability and inclusion formation; the dependences of surface supersaturation on the solution flow surrounding the crystal surface are analyzed in detail. The correlations between thickness of the solute boundary layer and translational velocity and distance are described. The roles of natural and forced convection in mass transfer under different conditions are discussed, with results showing that the effects of natural convection are significant only at low translational velocities. The Damkohler number is introduced to measure the significance of mass transport limitations in the solution system of 3D MGM crystal growth, where it implies that with the increase of translational velocity, the limitations in mass transport decrease. Comparisons with the traditional rotating-crystal method indicate that 3D MGM has advantages in terms of the distribution homogeneity of surface supersaturation. The model of steps moving on the prismatic face demonstrates that the step-train propagates more stably on the crystal surface when the 3D MGM is applied.

1. Introduction

Mass transport during solution-based crystal growth depends mainly upon two processes, i.e., convection and diffusion. High-quality crystals can be obtained if the mass transport depends completely on diffusion without convection. Nevertheless, extremely slow growth rates attributed to low diffusional rates hinder large-scale crystal. Wilcox [1] pointed out that even slight convection could strongly affect mass transport at the crystal/solution interface, thereby influencing the growth rate and morphological stability of the crystal surface.

A number of experimental and theoretical studies have shown that convection can enhance growth rates. However, it may also induce morphological instability of the crystal surface and resulting in step bunching and inclusions [2–6].

Chernov et al. [2] presented a typical relationship between solution flow and step bunching on the (001) face of ammonium dihydrogen orthophosphate (ADP) crystals and showed that the hillock slope where steps move in the same direction as the solution was rippled, i.e., step bunches were formed; on the opposite slope of the same hillock, however, where the steps and solution flow in opposite directions, no visible bunching was observed. Booth et al. [3] developed a real-time phase-shifting interferometer capable of imaging interfacial morphology to study the formation and evolution of solution flow-induced step bunches; results showed that bunching occurs when the solution flows in the same direction as the moving step. Chernov [4] pointed out that, besides the considerable importance of solution flow direction, the velocity of the solution flow exerts a significant influence on the height and width of the step bunch in determining the stability of the step advancement. Vekilov observed strong fluctuations in local growth rate, local slope (step density), and tangential step velocity on horizontal facets of protein lysozymes by high-resolution in situ interferometry and proposed that convection affects the effective

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macrostep height and fluctuation amplitude along the step path by altering the interfacial supersaturation distribution. If the direction of step motion is the same as that of convective flow, the fluctuation amplitude increases; otherwise, the counterflow dampens the fluctuations [5]. Smolsky [6] observed a special type of oriented inclusion by means of optical microscopy and X-ray topography and concluded that these inclusions are probably induced by morphological instability during high-velocity crystal growth.

Linear stability analysis has been applied to analyze morphological stability under different hydrodynamic conditions [7–10]. The vicinal face is unstable if the steps and fluid move in the same direction [7]. A shear flow (e.g., linear Couette flow or asymptotic suction profile) parallel to the crystal/solution interface and in the same direction as the step motion (negative shear) undermines interface stability [9], whereas a shear flow counter to the step motion enhances stability. In fact, the interface is absolutely morphologically stable under sufficiently large shear rates [10]. Potapenko [11] studied the morphological instability of a crystal surface and its relation with inclusion formation. This researcher pointed out that the process of inclusion formation may be divided into two stages: First, the steps bunch into macrosteps, after which, lateral instability of the steps moving at the vicinity of the leading edge of the macrostep develops under the influence of their diffusion field. This work demonstrated that the vicinal crystal face is morphologically stable regardless of perturbation if the solution flow is exactly reversible. The effect of oscillatory shear flow on step bunching haves also been analyzed [12], and modulation was revealed to either increase or decrease morphological stability, depending on the modulation amplitude and frequency.

As described above, the solution flow direction plays an important role in morphological stability. If the flow direction can be adjusted to directly contrast the step motion, morphological stability can be enhanced. Based on this idea, the rotating-crystal method, a typical approach applied to generate relative motion between crystals and a solution, is used during crystal growth from solution by rotating the crystals reversibly. Despite the many advantages of the rotating-crystal method, however, it also presents distinct disadvantages. For example, valleys are easily formed at the central portions of the crystal surface, and while these valleys can be restrained by adopting proper periodically reversal rotation, they cannot be completely eliminated. Such a phenomenon is believed to be associated with the gradient of supersaturation along the crystal face. The degree of supersaturation close to the edge is larger than that at the central regions of the crystal surface, thus regions near edges exhibit larger growth rates than regions closer to the crystal center. Moreover, reversible stirring does not mean a reversible shear rate over the whole crystal surface. Therefore, large parts of the crystal surface may remain unstable despite some regions showing stability. These highlight the fact that the rotating-crystal method presents obvious disadvantages when utilizing convection. As such, refinement of this conventional growth method is necessary.

The physical essence of flow-induced stability and instability described above is that mass transfer of the solute occurring at the vicinity of the crystal/solution interface is affected by flow. The stability or instability of some surface morphology depends strongly upon the surface supersaturation of crystals. However, determining the extent of surface supersaturation via in situ experimentation is difficult. Although Onuma et al. [13,14] previously reported the use of direct measurements to obtain surface supersaturation, such measurements cannot be carried out under actual growth conditions because of the complex geometry of the growth vessel and the rapid motion of crystals.

Numerical simulations of the flow and mass transfer are essential to provide an understanding of the surface supersaturation distribution. Zhou et al. [15,16] completed three-dimensional time-dependent flow simulations of potassium dihydrogen phosphate (KDP) crystal growth with crystals spinning up, spinning down, and maintaining steady rotation during growth and found that the flow exerts a great influence on crystal growth. Brailovskaya et al. [17] performed 2D simulations of the solution dynamics, including natural and forced convection, above the surface of growing KDP crystals and obtained the surface distribution of concentration and stream function. Robey and Maynes [18,19] executed three-dimensional time-dependent turbulent flow simulations of a rapid KDP single-crystal growth system and obtained the temporal and spatial evolutions of the shear stress and supersaturation distributions on the crystal surface as a function of crystal size, growth rate, and rotating rate. Liiri et al. [20] established a self-consistent model based on actual crystal growth conditions through introduction of a growth rate and surface reaction equation and use of CFX software to solve the flow velocity and solute boundary layer thickness around the crystal. Robey et al. [21] established the relation between step bending, rotation rate, and growth rate through a relatively simple model linking step propagation with the supersaturation distribution of the crystal surface; in this study, the "bending" of steps and the resulting "valleys" varied with the rotation rate. This method provides excellent guidance for studying the morphological stability of crystal surfaces through numerical simulations.

In the present paper, a new crystal growth method, namely, the three dimensional motion growth method (3D MGM) is proposed to effectively utilize convection and achieve enhanced morphological stability and mass transfer. Numerical simulations involving flow and mass transfer during the growth of a small KDP crystal are carried out. Surface supersaturation is described as functions of translational velocity and distance. Compared with the conventional rotating-crystal method, 3D MGM shows advantages in terms of the distribution homogeneity of surface supersaturation and morphological stability.

2. Physical and mathematical models

2.1. Physical model

As shown in Fig. 1a, a well-characterized KDP crystal with a prism size of $20 \times 20 \times 20\,mm^3$ and pyramid height of 10 mm is placed into a rectangular vessel measuring $120 \times 120 \times 120\,mm^3$. The vessel is fully filled with 8% supersaturated solution. Crystal motion begins at point 1 and follows the scheduled translational path during the entire growth process. During translations, the translational directions are parallel to *X*-, *Y*-, or *Z*-axis. The translational velocity *V* or translational distance *L* in different directions can be set separately; however, in the present simulation, *V* or *L* is constant regardless of the direction along which the crystal translates. Compared with crystals rotated periodically or reversely, this unique motion mode is believed to possess following advantages: First, the velocity of all regions on the crystal surface is equal since crystal motion involves translation instead of rotation. Second, a reversible shear flow parallel to the crystal surface may be formed to enhance morphological stability. Third, the transfer of solutes from the bulk solution to the crystal faces is homogenous because crystal faces with the same simple index experience the same hydrodynamic conditions. The main geometry difference between the present physical model and actual apparatus is that the crystal rod is neglected since this rod is rather thin and exerts little impact on solution flow. Acceleration and deceleration during translation are also neglected because of the low translational velocity, which means a short acceleration or deceleration time. Moreover, no pause is observed before the translational direction is changed. The crystal changes its