Crystal Growth Rate Enhancement Caused by Adhesion of Small Crystals

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In industrial crystallization, crystals are generally grown in a multicrystal system. Observation of the growth behavior of a crystal growing in a multicrystal system shows some interesting growth phenomena that cannot be explained only by well-known molecular-level growth models such as the BCF model or two-dimensional nucleation growth model (see for example Van der Eerden, 1993). A typical example is growth rate enhancement caused by the incorporation of "small crystals."

Toyokura et al. (1984, 1989) originally reported that the growth rate of a large seed crystal (a few mm in size) was higher in the presence of small crystals than without small crystals. They speculated that the growth rate enhancement was induced by adhesion of μm-level small crystals to the surface of the large seed crystal as was observed under an optical microscope. However, they did not propose a model to describe the enhancement mechanism.

On the other hand, Matsuoka and coworkers (Matsuoka and Tanishima, 1993; Matsuoka and Eguchi, 1993; Matsuoka et al., 1996) pointed out that the growth rate enhancement may be caused by incorporation of very small crystals ("microcrystals" in their articles) into "macrogrowth units," which cannot be observed under an optical microscope. Adhesion of μm-level small crystals was ineffective for their growth rate enhancement.

In this article, we present experimental evidence that shows adhesion of μm-level small crystals causes growth rate enhancement of a large seed crystal. We also discuss findings from observations using an atomic force microscope (AFM) that show what is happening on the surface of a large seed crystal after the adhesion of small crystals. Based on the results of observations under an optical microscope and AFM, we conclude that the adhesion of small crystals causes the formation of cracks on the surface of the large seed crystal and that these cracks produce active growth steps. Based on the results, we propose a macroscopic mathematical model that can explain the observed growth rate enhancement.

Experimental Studies

Preparation of seed crystals

Seed crystals used for *in situ* observations were prepared by growing spontaneously nucleated crystals slowly (12 ~ 24 h for KAP, 2 weeks for sodium chloride) at room temperature in a stagnant solution. The crystals had clean surface (macroscopically) and were 1 ~ 3 mm in length.

Observation under an optical microscope

In situ observations of the growth behavior of sodium chloride and KAP seed crystals were carried out using the apparatus shown in Figure 1a. The experimental setup consisted of a feed tank (2), metering pump (4), heat exchanger (5), nucleator (7), flow cell (9), and differential interference microscope (BHS, OLYMPUS, Japan) fitted with a CCD camera. Small crystals can be formed continuously simply by agitating the nucleator. Dimensions of the homemade flow cell are shown in Figure 1b. The seed crystal was mounted directly on the bottom of the cell using an epoxy adhesive to avoid vibration caused by fluid flow.

Aqueous solution of a desired concentration was stored in the feed tank. The solution temperature was maintained at 5 K higher than the saturation temperature. The solution from the feed tank passed through the heat exchanger, where the solution was supersaturated by cooling, and was continuously fed into the flow cell. The seed crystal in the cell was allowed to grow under two different conditions (in a clear solution or in the presence of small crystals). The seed crystal was first allowed to grow in a clear solution until stable growth was attained by passing the solution through "route 1" in Figure 1a. Next, the seed crystal was grown in the presence of small crystals by switching the solution flow to "route 2." When adhesion of a small crystal to the seed crystal surface was observed, the flow was switched back to route 1, and the seed crystal was again allowed to grow in a clear solution to avoid further adhesion of small crystals. Growth behavior of the seed crystal and adhesion of a small crystal were observed under a differential interference microscope. Growth conditions are given later.

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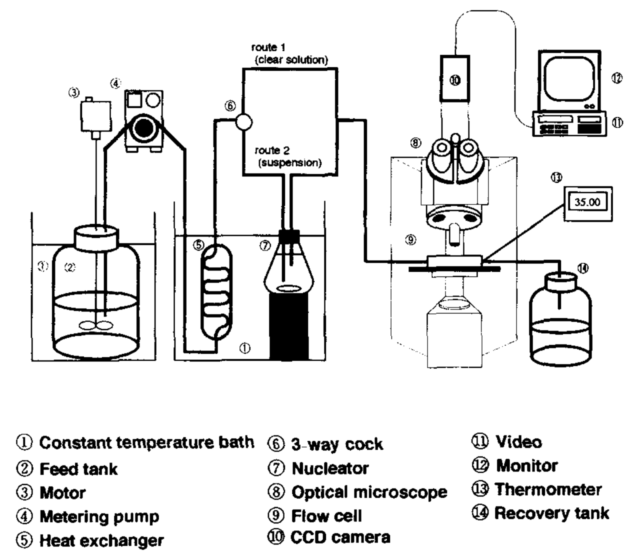
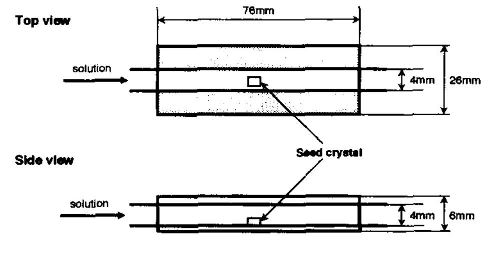


(a) Experimental set-up for insitu observation of crystal growth



(b) Flow cell

Figure 1. Experimental setup for *in-situ* observation of the growth of crystals (a) and flow cell (b).

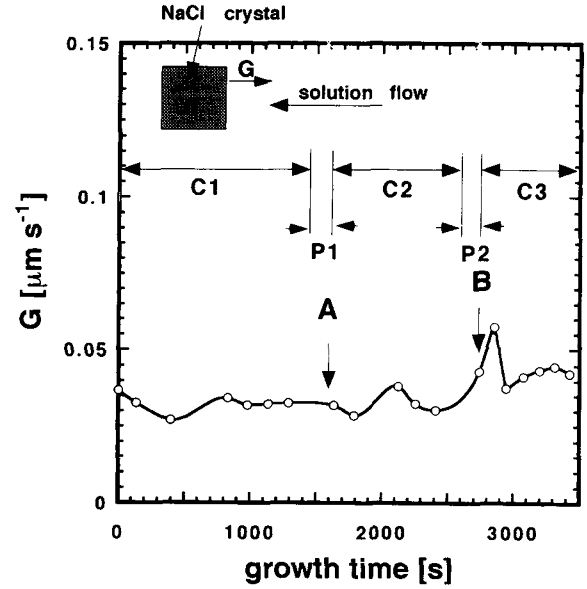


Figure 2. Transient growth rate of a sodium chloride seed crystal in clear solution (region C) and in the presence of suspended small crystals (region P).

A and B are the times when small crystals adhered to the seed crystal. $T_G = 308$ K; $C_s = 36.16\times10^{-2}$ kg/ka water; $\sigma = 4.23\times10^{-3}$; $U = 6.33$ cm$\cdot$s^{-1}.

Observation under an atomic force microscope

The surface topograph of a KAP seed crystal growing in solution was observed under an atomic force microscope (AFM, Nano Scope IIIa-D3000, Digital Instruments Inc., U.S.A.).

A KAP seed crystal was mounted with adhesive on a glass plate and was immersed in a KAP solution that was slightly supersaturated at a given room temperature. Higher supersaturation was avoided, because it made subsequent observation impossible with crystals nucleated preferentially on the surface of the cantilever of the AFM. During the initial period after the seed crystal was immersed in the solution, crystal growth was not observed through an optical microscope, which was fitted with our AFM due to insufficient supersaturation. However, evaporation of water in the solution led to a gradual increase in supersaturation, and the seed crystal eventually started growing. Some small crystals also formed spontaneously in the solution. When adhesion of a small crystal onto the surface of the seed crystal was observed through the optical microscope, the cantilever of the AFM was adjusted to the surface near the adhesion site to observe a microtopograph. However, we were not able to obtain the whole picture of the small crystal that had adhered to the surface of the seed crystal, because the dimensions of the small crystal were too large for AFM observation.

For the AFM observation, the seed crystal was grown in a stagnant solution at room temperature, because AFM observation in a flow system is very difficult due to the sensitivity of the cantilever to mechanical vibration.

Results and Discussion

Sodium chloride

Figure 2 shows a typical example of evolution of growth rate of a sodium chloride seed crystal in the clear solution (see regions C1, C2, C3 in the figure) and in the presence of small crystals (regions P1, P2). The illustration inserted in Figure 2 is a top view of the seed crystal showing the flow direction of the solution and the growth direction measured. When the seed crystal was grown in the clear solution, it exhibited stable growth for the initial period (marked by C1). At 1,454 s (start point of region P1), the seed crystal started to be grown in the presence of small crystals, and a small crystal about 45 μm in size adhered to the top surface of the seed crystal at point A. In this case, the growth rate of the seed crystal did not change even after adhesion. However, when another μm-level small crystal adhered to the front surface (point B: 2738 s), an increase in growth rate was observed. A photograph of the small crystal taken at this moment is shown in Figure 3a. The small crystal grew together with the seed crystal (3b). However, as the growth rate of the seed crystal was higher than that of the small crystal, the small crystal began to be buried into the seed crystal (3c). At 4,298 s (3d), the small crystal was completely buried, and the surface of the seed crystal became smooth again, appearing to

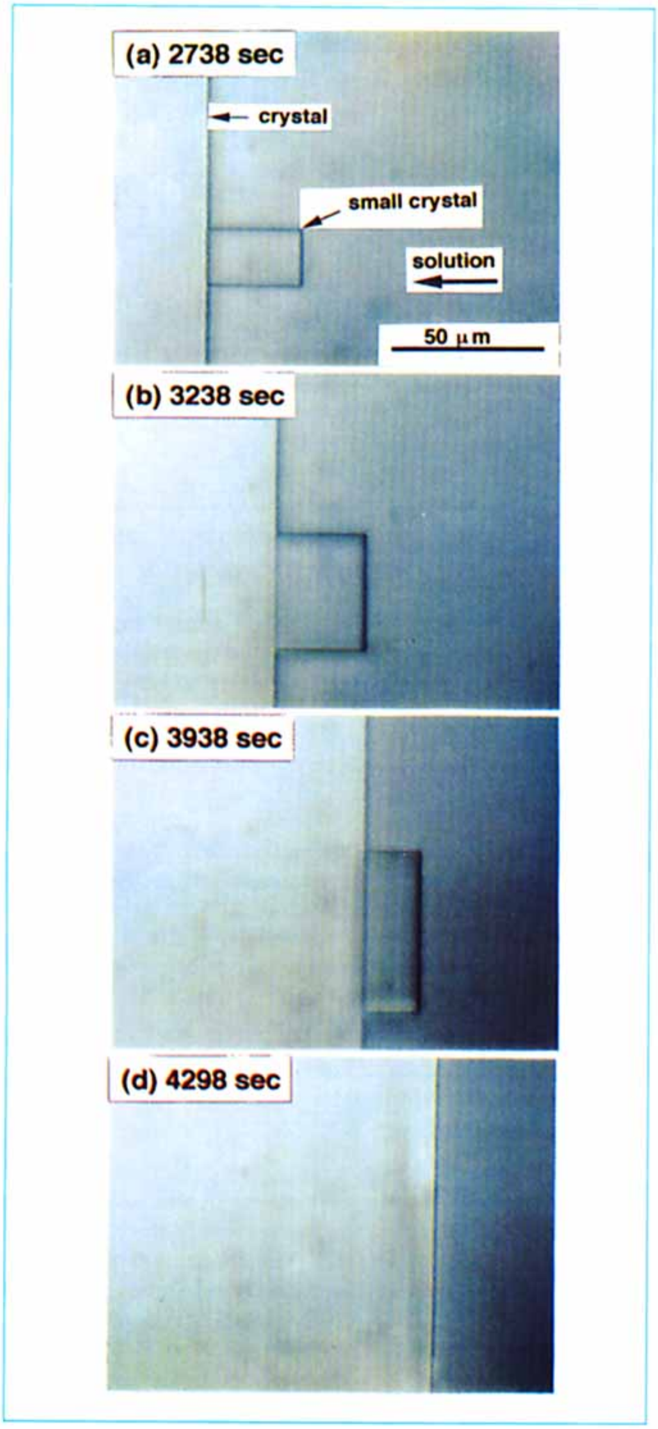


Figure 3. Sequence of optical microscopic pictures of the growth and submerging behavior of a small crystal adhered to the seed crystal whose transient growth rate is shown in Figure 2.

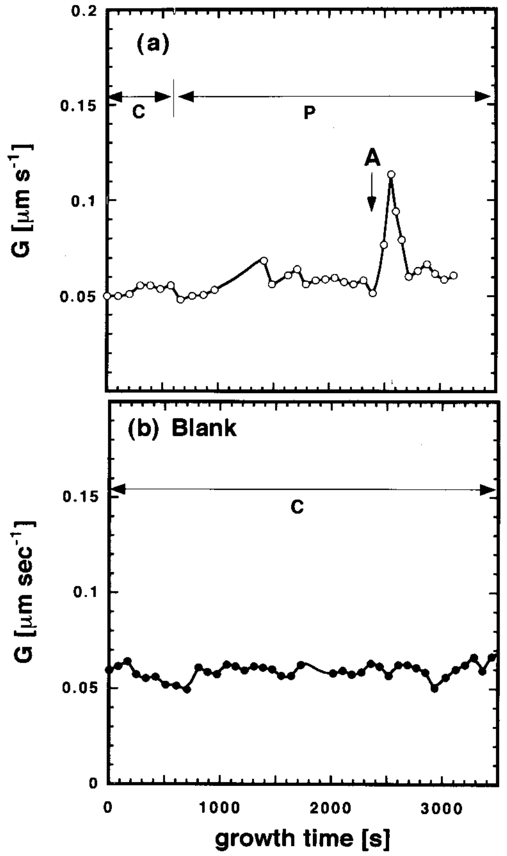


Figure 4. Transient growth rate of a sodium chloride seed crystal grown in clear solution (region C) and in the presence of suspended small crystals (region P) (a); transient growth rate of a sodium chloride seed crystal grown in clear solution (b).

A in Figure 4a is the time when a small crystal adhered to the seed crystal. $T_G = 308$ K, $\sigma = 4.23\times10^{-3}$, $C_s = 36.16\times10^{-2}$ kg/ka water, $U = 6.33$ cm·s^{-1}.

be a single perfect crystal. Compared to the time duration needed for the small crystal to be buried (1,560 s), the period of growth enhancement was very short (about 300 s) as shown in Figure 2. This suggests that growth enhancement is caused by a short-lived mechanism following the adhesion of a μm-level small crystal. The same trend as that in Figure 2 was also observed for another sodium chloride seed crystal (see Figure 4a). In this case, adhesion of a μm-level small crystal caused a more drastic growth rate enhancement compared to the case in Figure 2. This adhesion effect can be seen by a comparison with blank test data (Figure 4b). In the absence of small crystals (blank test), a seed crystal of sodium chloride maintained a constant growth rate for a long time period.

We measured the growth rates of more than 80 sodium chloride crystals. The extent of growth rate enhancement varied from crystal to crystal. Easily suspected factors such as supersaturation, growth rate dispersion among original seed crystals (initial growth rates), direction of adhered small crystals, and size of the small crystal cannot explain this scattering of data. Further investigation is needed to solve this scattering problem. Still, it is of interest that adhesion of μm-level small crystals enhances the growth rate of a seed crystal. Although we showed only temporal enhancement examples in Figures 2 and 4a, some seed crystals showed a continuously enhanced growth rate due to the adhesion of a small crystal. Moreover, adhesion of small crystals enhances not only the

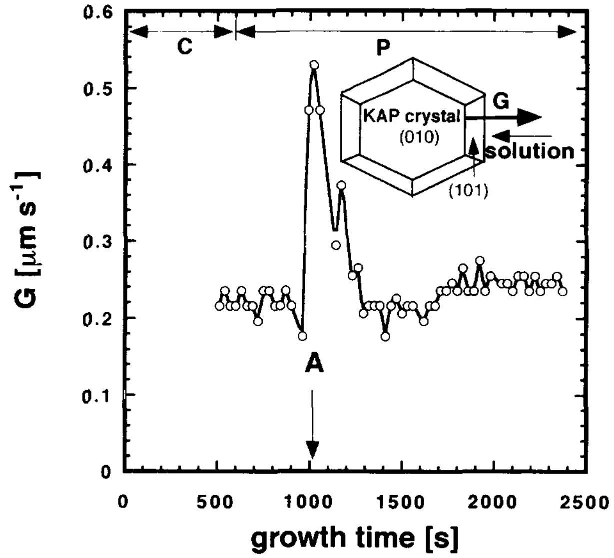


Figure 5. Transient growth rate of a potassium hydrogen phthalate seed crystal in clear solution (region C) and in the presence of suspended small crystals (region P).

A is the time when a small crystal adhered to the seed crystal. $T_G = 308$ K, $\sigma = 9.13\times10^{-2}$, $C_s = 14.32\times10^{-2}$ kg/ka water, $U = 9.45$ cm·s^{-1}.

growth rate of the crystal surface concerned but also the growth rate of other adhesion-free surfaces.

The following question arises: Is this growth enhancement a special phenomenon that can be observed only in the case of sodium chloride? In order to answer this, we present results of growth experiments on another system (potassium hydrogen phthalate-water) in the next section.

Potassium hydrogen phthalate (KAP)

Figure 5 is a typical growth behavior observed for a KAP seed crystal. The morphology of the KAP seed crystal used in this study can be seen in the figure. In this system, we measured the advancement rate of the edge line intersected by the (101) and (010) faces as the growth rate. It can be clearly seen that adhesion of a μm-level small crystal caused a temporal growth rate enhancement of the KAP seed crystal.

How did a μm-level small crystal act as a growth rate accelerator? Observation by an optical microscope could not show what was happening after adhesion of the small crystal, and therefore an atomic force microscope (AFM) was used to observe detailed surface topography of the crystal growing in solution. Figure 6 shows a typical sequence of AFM pictures of a KAP seed crystal taken near the adhesion site. A μm-level small crystal adhered to the edge of the (010) face of the seed crystal. Just after adhesion of the small crystal, new dense growth steps of approximately 2 to 10 nm in height appeared (Figure 6a). Before adhesion, such dense steps were not observed, although some growth steps with the same step height and step advancement velocity as those in Figure 6 were observed. The biggest difference between before and just after adhesion is the step density. After 30 s of 6a, step spacing gradually became wider. Finally at 6c, the step density returned to the original level. Appearance of these short-lived, dense steps may be the main cause of the temporal growth rate enhancement seen in Figure 5. Formation of short-lived, dense steps by adhesion of small crystals was also observed on the (101) face.

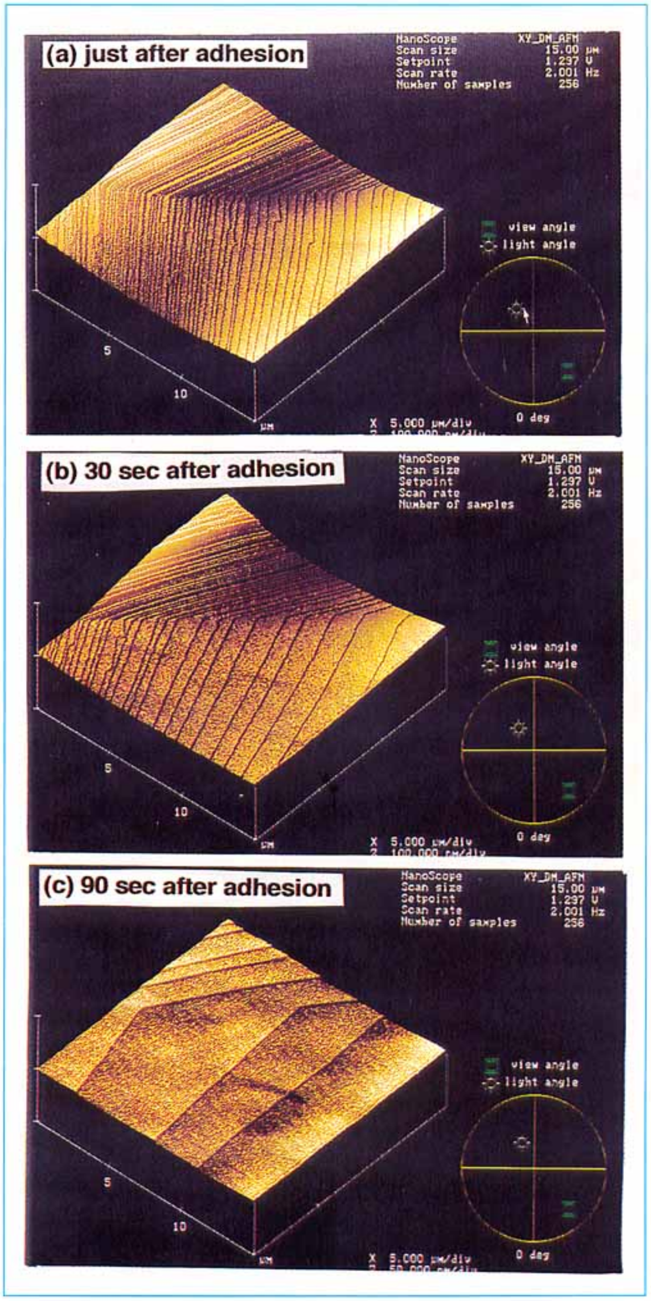


Figure 6. Sequence of atomic force (AFM) microscopic pictures of the site near the adhesion position at room temperature (298 K).

15×15 μm scan, AFM mode = tapping mode, Scan rate = 2.001 Hz.

Based on the experimental results described above, in the next section we discuss the growth rate enhancement mechanism induced by adhesion of a μm-level small crystal.

Crystal growth rate enhancement model

Here is a summary of some conclusions drawn from the experimental results described in the previous two sections (sodium chloride and KAP).

- Adhesion of a μm-level small crystal causes temporal growth rate enhancement of a seed crystal.
- Adhesion of a small crystal enhances not only the growth rate of the crystal surface to which the small crystal has adhered but also the growth rate of other adhesion-free surfaces.
- Adhesion of small crystals causes a temporal increase in step density.

These results suggest that the mechanism of growth rate enhancement by adhesion of a μm-level small crystal may be as follows. Basically, the original seed crystal grows by a step-flow (layer-by-layer) mechanism in clear solution. When a small crystal adheres to the surface of a seed crystal, some mechanical stress may be induced during incorporation due to the mismatch of lattice orientation. Hence, cracks may form on the crystal surface (randomly). Cracks can form not only on the surface to which the small crystal has adhered but also on other adhesion-free surfaces. From the cracks, new dense growth steps are generated. The steps have a short life due to bunching and coalescence among them. Thus, the step density soon returns to that of the original seed crystal. Based on these hypotheses, we propose the following simple mathematical model.

For a stepped surface, the crystal growth rate G (μm/s) can be expressed as

$$G(x,y,t) = h(x,y,t)\cdot v(x,y,t)\cdot \Gamma(x,y,t), \tag{1}$$

where $h(x, y, t)$ is the step height (μm), $v(x, y, t)$ is the step velocity (μm/s), and $\Gamma(x, y, t)$ is the step density (number/μm^2). In the case of a microscopic or mesoscopic growth model, $v(x, y, t)$ and $\Gamma(x, y, t)$ must be expressed as a function of surface position (x, y) and time t (s). In our case, however, the growth rate is needed only on a macroscopic level. In such a case, $\Gamma(t)$ can be averaged out over a surface area, and therefore

$$G(t) = h(t)\cdot v(t)\cdot \Gamma(t). \tag{2}$$

In Eq. 2, we selected step density as the most important factor influenced by adhesion of small crystals, based on the results of AFM observation (Figure 6). Step velocity and step height are not influenced by the adhesion of small crystals. Let Γ_{original} be the step density of the original surface of a seed crystal and Γ_{new} be the density of the step formed by adhesion of small crystals. Then, the resultant step density Γ is

$$\Gamma(t) = \Gamma_{\text{original}}(t) + \Gamma_{\text{new}}(t). \tag{3}$$

The growth rate becomes

$$G(t) = h(t)\cdot v(t)\cdot[\Gamma_{\text{original}}(t) + \Gamma_{\text{new}}(t)]. \tag{4}$$

The balance equation of the density of steps formed by adhesion of small crystals is

$$\frac{d\Gamma_{\text{new}}(t)}{dt} = B(t) - D(t), \tag{5}$$

where B is the rate of formation of a new step caused by crack formation at the surface (number/μm^2/s), and D is the death rate of a step due to coalescence between steps (number/μm^2/s). To solve Eq. 5, B and D must be expressed as a function of time and/or step density. Here we assume $B(t)$ can be expressed simply as

$$B(t) = \alpha \exp[-k\cdot(t-\tau)^2]. \tag{6}$$

This means the rate of formation of new steps increases exponentially in the initial period after adhesion. After τ, however, the rate decreases with time. On the other hand, $D(t)$ is considered to be as follows. Just after the adhesion of a small crystal, death of a step due to factors such as coalescence do not occur easily because of the lower level of step density. However, the frequency of death increases with an increase in the step density over time. Thus, $D(t)$ is

$$D(t) = \beta\cdot\Gamma_{\text{new}}(t) \quad (\text{when } \Gamma_{\text{new}} \gg \Gamma_{\text{original}}). \tag{7}$$

By substituting Eqs. 6 and 7 into Eq. 5, we obtain the final form of step density balance

$$\frac{d\Gamma_{\text{new}}(t)}{dt} = \alpha \exp[-k\cdot(t-\tau)^2] - \beta\cdot\Gamma_{\text{new}}(t) \tag{8}$$

$$\text{I.C.} \qquad \Gamma_{\text{new}}(0) = 0 \tag{9}$$

The solution of Eq. 8 with initial condition (Eq. 9) is easily obtained as

$$\Gamma_{\text{new}}(t) = \frac{1}{2\sqrt{k}}\left[\alpha\sqrt{\pi}\cdot\operatorname{erf}\left(\frac{\beta+2k\tau}{2\sqrt{k}}\right)\cdot\exp(-\beta t) \cdot\exp\left(\frac{(\beta+4k\tau)\cdot\beta}{4k}\right) - \alpha\sqrt{\pi}\cdot\operatorname{erf}\left(\frac{\beta+2k\tau-2kt}{2\sqrt{k}}\right) \cdot\exp\left(\frac{(\beta+4k\tau-4kt)\cdot\beta}{4k}\right)\right] \tag{10}$$

Suppose step height h, step velocity v, and step density of original seed crystal Γ_{original} are constant. By substituting Eq. 10 into Eq. 4, we get the final growth rate equation

$$G(t) = h\cdot v\cdot\left\{\Gamma_{\text{original}} + \frac{1}{2\sqrt{k}} \times\left[\alpha\sqrt{\pi}\cdot\operatorname{erf}\left(\frac{\beta+2k\tau}{2\sqrt{k}}\right)\cdot\exp(-\beta t)\cdot\exp\left(\frac{(\beta+4k\tau)\cdot\beta}{4k}\right) - \alpha\sqrt{\pi}\cdot\operatorname{erf}\left(\frac{\beta+2k\tau-2kt}{2\sqrt{k}}\right)\cdot\exp\left(\frac{(\beta+4k\tau-4kt)\cdot\beta}{4k}\right)\right]\right\} \tag{11}$$

In Figure 7, we compare the measured growth rates of KAP

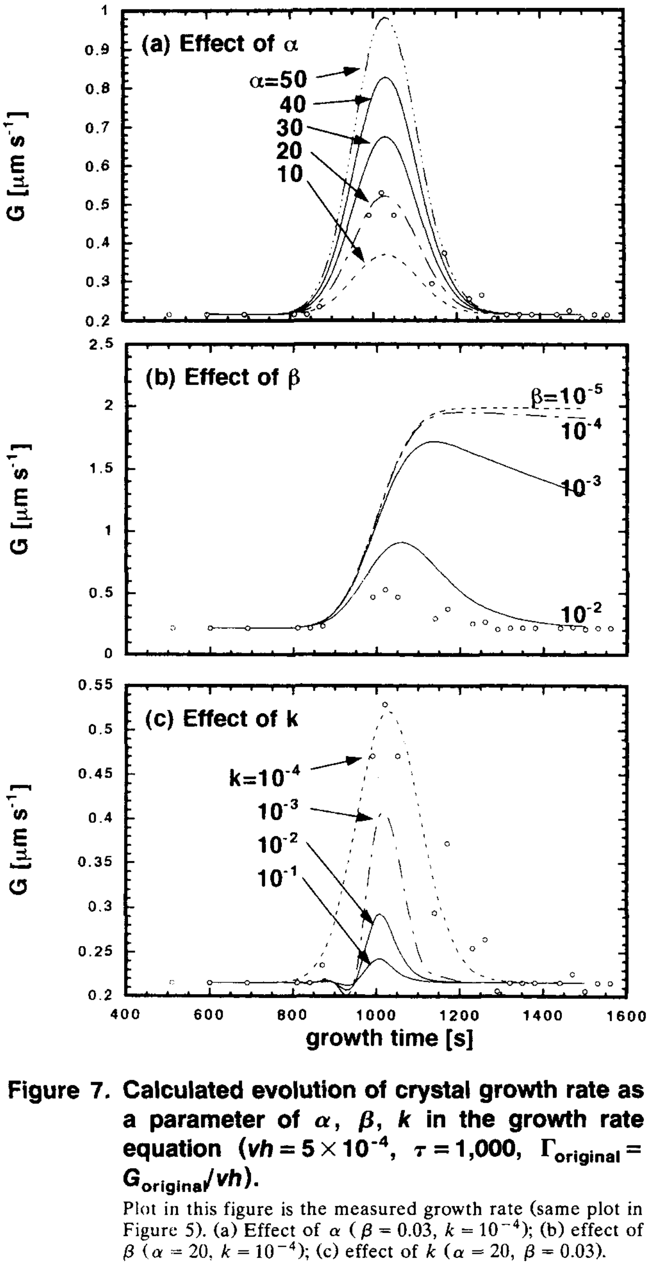


Figure 7. Calculated evolution of crystal growth rate as a parameter of α, β, k in the growth rate equation ($vh = 5 \times 10^{-4}$, $\tau = 1{,}000$, $\Gamma_{\text{original}} = G_{\text{original}}/vh$).

Plot in this figure is the measured growth rate (same plot in Figure 5). (a) Effect of α ($\beta = 0.03$, $k = 10^{-4}$); (b) effect of β ($\alpha = 20$, $k = 10^{-4}$); (c) effect of k ($\alpha = 20$, $\beta = 0.03$).

(Figure 5) with calculated values of G, giving various values to the unknown parameters in Eq. 11. The effect of α can be seen in Figure 7a, that is, an increase in growth enhancement with an increase in α. When $\alpha = 20$, the calculated values of G agree well with all the measured values of G. Of course, there are other sets of parameters (α, β, k) that satisfy the observed evolution of growth rate. We do not know which set is correct yet. The effect of β, which can be seen in Figure 7b, is very interesting. A decrease in β leads to continuous growth rate enhancement, which was sometimes observed experimentally. Figure 7c shows the effect of k.

Relevance of crystal growth rate in industrial crystallizers

What will happen in an industrial crystallizer when growth rate enhancement occurs due to adhesion of suspended small crystals? We can expect two typical situations, depending on the ratio of the number of small crystals n_s to the number of larger crystals n_L.

When $n_s > n_L$, adhesion of small crystals to the surface of large crystals would occur frequently, and, therefore, temporal growth rate enhancement would occur frequently and repeatedly on growing crystals. This frequent temporal growth rate enhancement would lead to an increase in the average growth rate of the crystals. On the other hand, when $n_s < n_L$, adhesion of small crystals onto large seed crystals would rarely occur, and, therefore, the crystal would show fluctuations in growth rate. This may be related to the well-known crystal growth rate dispersion (GRD).

Here, we try to link the growth rate enhancement shown in this study with the recognized GRD. There are two explanations for GRD. One is the difference in surface topographic characteristics (such as the number of screw dislocations and/or 2-D nuclei, and so on) among the crystals. We can easily imagine that a crystal with a higher density of dislocations and/or 2-D nuclei can grow faster than can a dislocation- and 2-D nuclei-free crystal. The other explanation, which has been proposed recently, is the difference in the levels of stress in a crystal (Huitema and van der Eerden, 1996; Larson and Jones, 1995; Tanneberger et al., 1996; Van der Heijden, 1992; Zacher and Mersmann, 1995). When stress accumulates in a crystal, the chemical potential of the crystal is increased, resulting in a decrease in the driving force for crystal growth, which is defined as the difference between the chemical potential of the solution and the solid. This leads to a decrease in the crystal growth rate. If the latter case did occur in this study, then the decrease in the crystal growth rate following the adhesion of a small crystal must have been due to some stress induced by a mechanism such as the mismatch of lattice orientation when a small crystal adhered to the surface of a seed crystal. This would tend to reduce the rate of crystal growth. However, the growth rate in the present study was enhanced by the adhesion of small crystals. This conflict may be possibly explained as follows. Although some stress accumulates in the crystal due to adhesion of a small crystal, the accumulated stress is relaxed when some cracks emerge on the surface of the crystal due to adhesion. The accumulation-formation-relaxation processes progress rapidly. Consequently, the crystal growth rate can be enhanced after adhesion of a small crystal by an increase in active growth sites (step).

Conclusions

Optical microscopic and atomic force microscopic observation of the growth of sodium chloride and KAP large crystals led to the following conclusions:

- The growth rate of large seed crystals is enhanced by adhesion of μm-level small crystals. The growth rate enhancement is usually a temporal phenomena.
- Adhesion of small crystals enhances not only the growth rate of crystal surface involved, but also the growth rate of other adhesion-free surface.
- Dense steps are formed on the surface of the large seed crystal just after adhesion of a small crystal. This may be the main cause of the temporal enhancement in growth rate.

Acknowledgment

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Notation

C = solution concentration, kg solute/kg water
C_s = saturation concentration, kg solute/kg water
ΔC = supersaturation ($= C - C_s$), kg solute/kg water
k = kinetic coefficient defined in Eq. 6
T_G = growth temperature, K
U = flow rate of solution in the growth cell, m/h
σ = supersaturation ratio ($= \Delta C/C_s$)
τ = time when formation rate of new step becomes maximum, s

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