

Effect of Growth Rate History on Current Crystal Growth: A Second Look at Surface Effects on Crystal Growth Rates

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ABSTRACT: The effect of a crystal's growth rate history on the current growth behavior was investigated as a cause of crystal growth rate dispersion (GRD), which is a significant problem in crystallizer design and modeling. The solute used in the experiments was sucrose, a high production commodity still crystallized mainly in batch crystallizers, where GRD is most significant. The results show that the growth history of a crystal has a significant effect on the crystal growth rate of that crystal. In particular, a history of rapid crystal growth under high supersaturation causes a roughening of the crystal surface, apparently due to poor surface integration, and subsequent growth occurs at lower rates than would be expected without this growth history. The process of crystal surface healing occurs at low levels of supersaturation over periods of several hours of growth and results in the crystals again reaching their normal growth rate levels. The growth layer formed to heal the surface of the crystal is greater than 100 μm thickness, far in excess of the scale of the apparent surface roughness. This study shows that the crystal perfection near the growing surface of the crystal may be a more significant indicator of crystal growth rate than the overall average perfection in the entire crystal.

Introduction

Crystal growth rate dispersion is a phenomena encountered in crystallization that describes how seemingly identical crystals in the same conditions of temperature, pressure, composition, and flow grow at different rates. Since the initial study of White and Wright¹, a large amount of research has been conducted to determine the causes and mechanisms of GRD, but the mechanism responsible for the phenomenon is still little understood. The mechanism initially proposed involved a variable amount of molecular scale surface roughness between different crystals, due to a varying surface concentration of screw dislocations. From modern models of surface integration kinetics, such as BCF theory, it was assumed that the growth rate of an individual crystal was related to the number of screw dislocation sites on its surface. However, the idea that molecular scale surface roughness is relevant to the study of GRD was discounted by Herden and Lacmann² in their study of potassium nitrate. The relation between the overall lattice perfection of a crystal and its growth rate was proposed by Ristic et al.,³ and subsequent studies have both agreed (i.e., Mitrovic,⁴ Ristic et al.,⁵ and Zacher and Mersmann⁶) and disagreed (i.e., Herden and Lacmann² and Harding et al.⁷) with their conclusions. Herden and Lacmann² suggested that there is no correlation between face-specific growth rates of KNO and Laue quality. The difficulty in correlating Laue quality with growth rates may be explained by the fact that the Laue quality is determined for the whole crystal, while the growth rate is face-specific and related to surface features only. A correlation between Laue quality and growth rate is possible, but it is unlikely that it is sufficient to describe the mechanism or cause of GRD.

Tanneberger et al.⁸ observed the influence of pulse changes in supersaturation ($\sigma_1:\sigma_2:\sigma_1$ with σ_2 either more than or less than σ_1) on the growth rate of potassium alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$). The results showed that the growth rate decreases with decreasing supersaturation σ_2 and increases with increasing supersaturation σ_2 , but it does not return to the previous value after the second supersaturation change (returning to σ_1) in a short time period. Herden and Lacmann suggested that the effect might be explained by a change of the surface structure of the crystal, which is then responsible for a change in growth rate.² This situation could be quite important during the nucleation period in a batch crystallizer; the initial nuclei form at a higher supersaturation than later nuclei, which may relate to differences in initial growth rates for apparently identical nuclei. If the suspension of a continuous crystallizer was not sufficiently mixed, a similar mechanism could be created by spatial variation in the solute concentration. The current study, therefore, investigates whether the growth rate history of individual crystals is related to crystal growth rate dispersion.

Experimental Procedures

Materials. Solutions were produced from commercial grade white sugar of approximately 99.9% purity (Mitr Phol, Thailand) and water treated by reverse osmosis. Sucrose seed crystals were taken from the same source, with a narrow seed size distribution achieved by selecting crystals of approximately the same size using inspection under a microscope. Seed crystals of unusual shape or containing obvious surface features were excluded. The crystal size distribution of a seed sample used in the batch crystallization study is shown in Figure 1.

Apparatus. Crystallization experiments were performed in both a single-crystal growth cell and a batch crystallizer. The single-crystal growth cell is depicted in Figure 2. A single crystal was mounted between two pins, at the center of the

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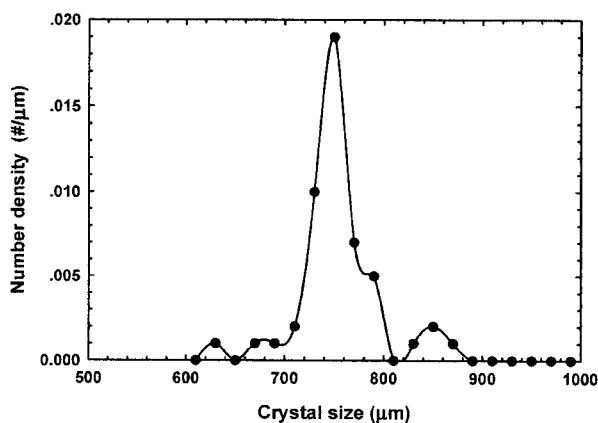


Figure 1. Example crystal size distribution of seed crystals used in the batch crystallization experiments.

pipe cross-section, in a flow of mother liquor. The pins and supports were designed to minimize their effect on the flow of solution. The crystal holder was positioned toward the end of the pipe to minimize end effects on the fluid flow at the crystal. The cell may be used for growth in stagnant solution and where the effect of a quantitatively known solution velocity is required. Temperature in the system was maintained by flow of water from a constant-temperature bath through jackets around the apparatus.

The suspension in the 2-L batch crystallizer was agitated by a centrally located, four-blade impeller driven by an overhead mixer operating at 500 rpm. A constant crystallization temperature was maintained by immersion of a heating coil connected with a constant-temperature bath. Samples were periodically obtained from the crystallizer and analyzed for size distribution.

Crystal Size and Growth Rate Determination. A sample of at least 30 crystals was used to determine the crystal size distribution in the batch crystallizer. The crystals were dried using vacuum filtration and had residual solution adhering to the surface removed using a lint-free tissue. Crystals were individually examined under a microscope that contained a calibrated scale in its lens. The scale was calibrated using standard sized wires and crystals of various sizes that had been measured by a digital micrometer. The method was confirmed to be reliable by comparing the results to sizing crystals directly with a digital micrometer. The method had a reproducibility of $\pm 5.0 \mu\text{m}$. Individual crystals from the pipe cell crystallizer had their size determined in an identical procedure.

The growth rate of individual crystals in the pipe cell crystallizer was determined by calculation of the slope of the line representing their crystal size against crystallization time, with growth rate determinations based on three to five size determinations. The average value of the coefficient of deter-

mination (R^2) for these lines was 0.9984, indicating that the crystal growth followed the constant crystal growth model closely and that the crystal sizing results were quite accurate. Average 90% confidence intervals on the growth rate of individual crystals in the growth cell were $\pm 0.16 \mu\text{m}/\text{min}$. The mean crystal growth rate in the batch crystallizer was found by determining the slope of a plot of the number mean crystal size versus time. Confidence intervals for the mean growth rate were calculated based on the average 90% confidence interval on the slope of the plots, which was $\pm 0.18 \mu\text{m}/\text{min}$. An example set of distributions is shown in Figure 3. A plot of the number mean crystal size versus time for this example is shown in Figure 4.

Determination of the Effect of Growth Conditions on Surface Roughness. Experiments were performed by observation of the surface of each sucrose crystal grown in the pipe-cell crystallizer under different levels of supersaturation. Crystals were grown at 1.50, 2.20, 3.60, and 5.10% relative supersaturation at conditions where the growth rate was integration controlled. Photographs of individual crystals before and after growth were taken using a digital camera attached to a microscope. SEM micrographs were also prepared for the product crystals (after growth). It is noted that the current experiments were investigating surface roughness on a microscopic scale, not at the molecular level. Molecular surface roughness is related to effects such as molecular dislocations in the crystal and thermodynamic effects related to the surface entropy factor. Microscopic surface defects are most likely caused by poor lattice formation during large-scale surface nucleation or cluster incorporation.

Determination of the Effect of Growth History on Current Crystal Growth. Experiments were carried out in a 2-L batch crystallizer by measuring the population average growth rates of sucrose crystals at different supersaturation, after initially being grown at the same supersaturation. For example, a group of crystals grown for 3 h in 1.50% relative supersaturation was separated into four groups, which were subsequently grown at 1.50, 2.20, 3.60, and 5.10% relative supersaturation.

Other experiments to study the effect of growth rate history on current crystal growth were performed in the pipe-cell crystallizer. These experiments had the crystal grown for 3 h under an initial supersaturation (σ_1), followed by growth at a second supersaturation (σ_2), after which the supersaturation was returned to the initial supersaturation (σ_1). The value of the initial supersaturation was fixed at 0.70% relative supersaturation; intermediate values were varied at 1.50, 2.20, 3.60, and 5.10% relative supersaturation. To study the time required for healing, a second series of experiments with three concentration jumps ($\sigma_1;\sigma_2;\sigma_3;\sigma_2$) was also performed.

Results and Discussion

Effect of Growth Conditions on the Microscopic Surface Roughness. Experiments were performed in the pipe cell crystallizer to determine if growth history

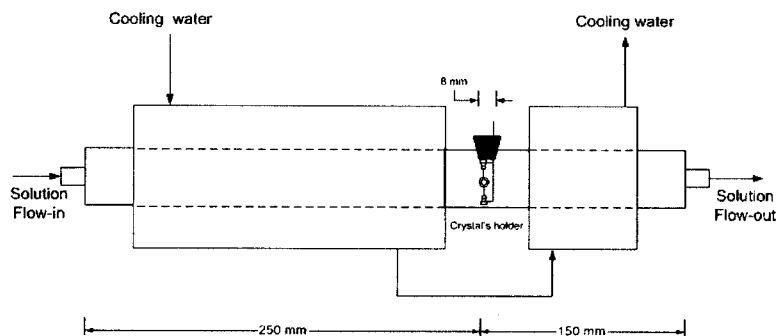


Figure 2. Pipe cell crystallizer used to measure crystal growth under well-determined flow conditions.

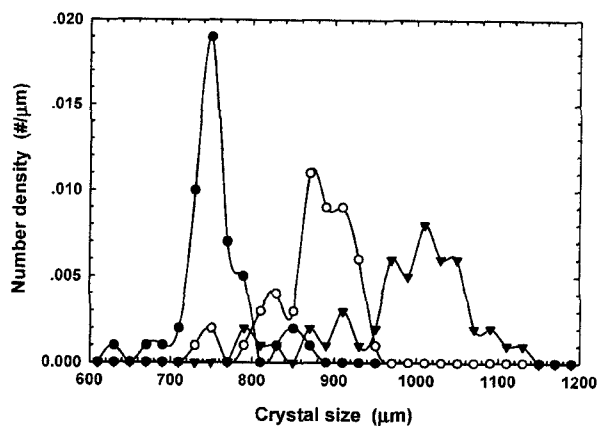


Figure 3. Crystal size distributions in a batch crystallization experiment: ● seed crystals; ○ 60 min; ▼ 120 min.

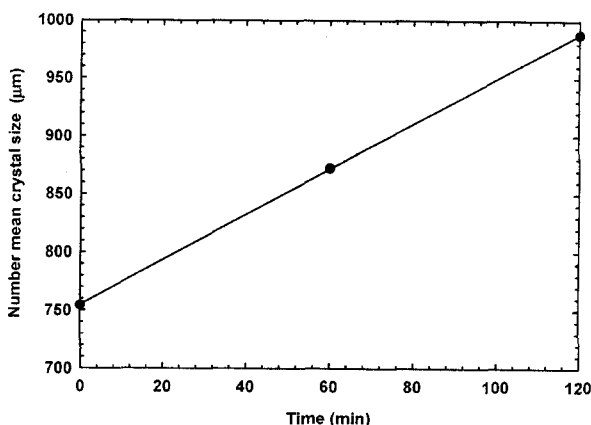


Figure 4. Change in the number mean crystal size with respect to time in a batch crystallization experiment.

had an appreciable effect on the surface appearance of crystals. The experiments were to be carried out under surface integration controlled conditions, and so an initial experiment was performed to determine the limit of the solution flow in the crystallizer that results in surface integration controlled crystal growth of sucrose. Surface integration controlled growth may be assumed if an increase in the relative velocity of the crystal and the solution (and therefore the solution velocity relative to the mounted crystal) does not increase the crystal growth rate. The effect of solution flow on the mean growth rate of crystals in the pipe cell crystallizer is illustrated in Figure 5. A flow velocity of 300 mL/min was chosen for all other experiments in the pipe cell crystallizer.

The experiments demonstrated that the growth history had significant effect on the surface roughness of the crystal, with crystals grown more quickly at higher supersaturation having a surface that was significantly rougher on a microscopic level than the seed crystals they were grown from. A sample set of results is shown in Figure 6. The seed crystals were randomly chosen and because of this had a variable amount of surface roughness at the beginning of the crystal growth. The results suggest that crystals grown at lower supersaturation became smoother, while those at the higher supersaturation levels had progressively rougher sur-

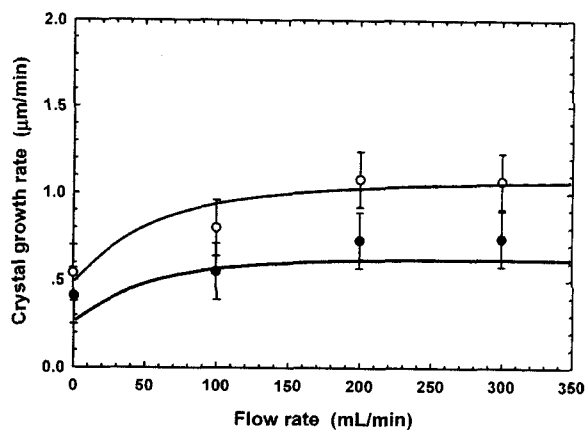


Figure 5. Effect of flow rate on the mean crystal growth rate of sucrose crystals in the pipe-cell crystallizer: ● 2.20% relative supersaturation; ○ 3.60% relative supersaturation.

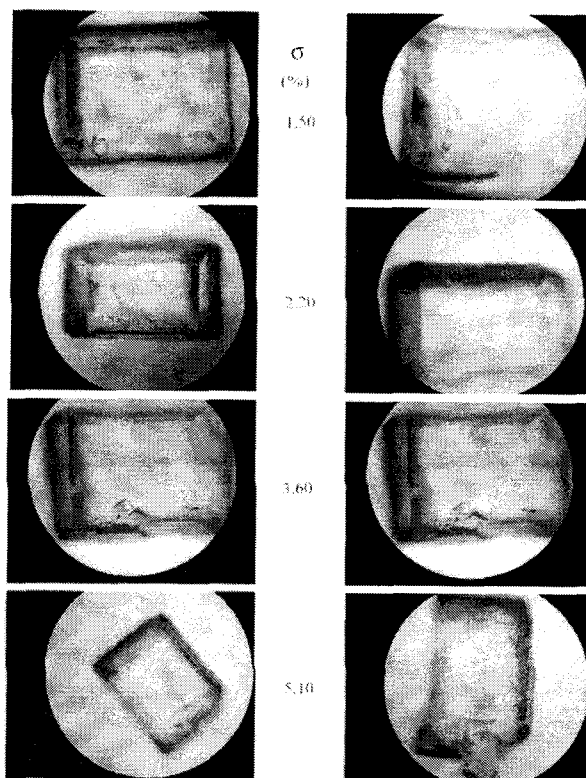


Figure 6. Effect of supersaturation during crystal growth on the surface roughness of sucrose crystals.

faces. SEM micrographs of the products crystals of 2.20 and 5.10% relative supersaturation are shown in Figure 7 for comparison. The roughness appears to be the results of imperfect integration of growth clusters onto the surface of the crystals, which will be discussed in the next section.

Effect of Growth Rate History on Current Crystal Growth. The effect of growth rate history on current crystal growth rates was studied through the crystallization of sucrose in a batch crystallizer. Initial experiments were performed to determine the minimum agitation rate in the batch crystallizer that resulted in

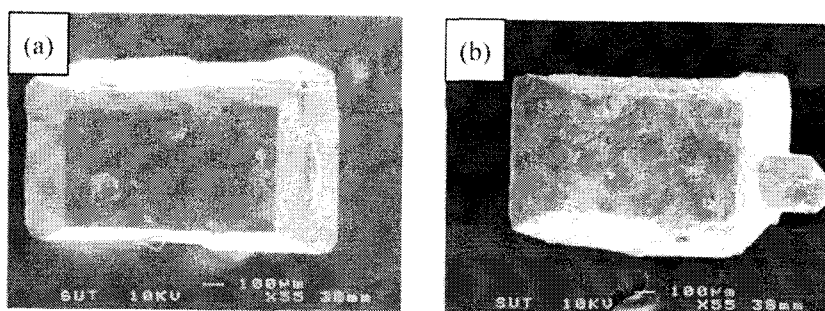


Figure 7. SEM micrographs of the surface of a sucrose crystal (a) after growth at 2.2% relative supersaturation and (b) after growth at 5.1% relative supersaturation.

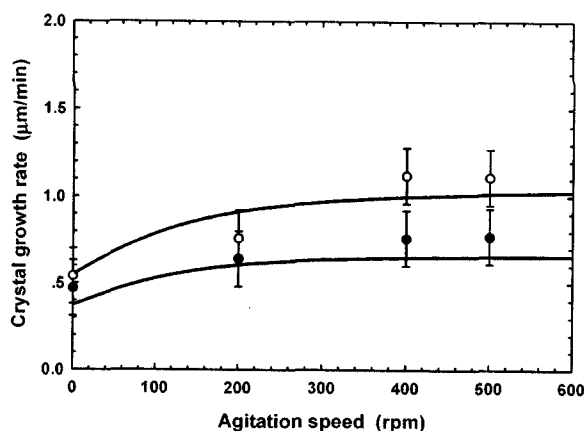


Figure 8. Effect of agitation rate on the mean crystal growth rate of sucrose crystals in the batch crystallizer: ● 2.20% relative supersaturation; ○ 3.60% relative supersaturation.

Table 1. Effect of Crystal Growth History on Current Crystal Growth Rates of Sucrose Crystallized in a Batch Crystallizer

growth at σ_1		growth rate at σ_2 (%): G_2 ($\mu\text{m}/\text{min}$)			
σ_1 (%)	G_1 ($\mu\text{m}/\text{min}$)	$\sigma_2 = 1.50$	$\sigma_2 = 2.20$	$\sigma_2 = 3.60$	$\sigma_2 = 5.10$
1.50	0.48	0.46	0.72	1.19	2.00
2.20	0.74	0.66	0.76	0.92	1.60
3.60	1.25	0.54	0.76	0.94	1.38
5.10	1.95	0.26	0.57	0.84	1.91

surface integration controlled crystal growth. In batch crystallizers, the crystal growth may be assumed to be surface integration controlled at the point where additional increases in agitation speed (resulting in increased relative velocities between crystals and the solution and enhanced diffusion) do not increase the crystal growth rate. It was desired to operate the crystallizer under integration-controlled growth but not use impeller speeds high enough to damage the crystals being studied. Figure 8 demonstrates the effect of impeller speed on the mean crystal growth rate for both 2.20 and 3.60% relative supersaturation. An impeller speed of 500 rpm was chosen for the crystal growth rate studies.

Results demonstrating the effect of growth history on current crystal growth rates are summarized in Table 1. The diagonal of the table represents growth at constant conditions for 6 h, and these results showed approximately constant rates for the two periods (for instance, 1.95 $\mu\text{m}/\text{min}$ for the first period of 3 h and 1.91

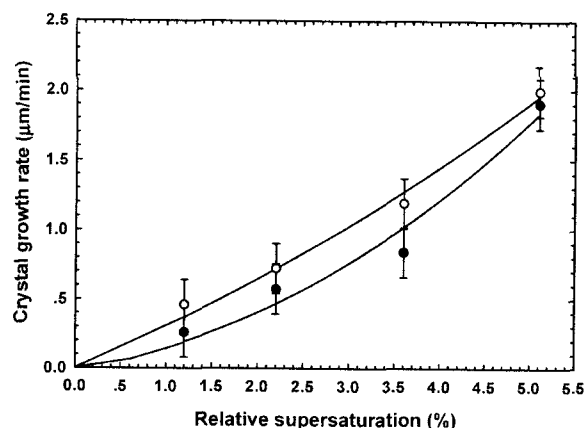


Figure 9. Effect of growth history of sucrose crystals on their current crystal growth. Previous crystal growth under: ● 5.10% relative supersaturation; ○ 1.50% relative supersaturation.

$\mu\text{m}/\text{min}$ for the second period of 3 h at 5.10% relative supersaturation) with the exception of the system at 3.6% supersaturation: the cause for this discrepancy is not known, but other experiments have shown this to be a rare occurrence, likely due to the initial rate being at the high end of the statistical uncertainty limits and the later value being at the low end of the uncertainty limits. The data above the diagonal represents experiments where the second period of growth occurred at higher supersaturation than the initial period and vice versa for the data below the diagonal.

There is a clear relation whereby crystals initially grown at a low initial supersaturation have a higher growth rate during the second period of growth than the crystals initially grown at a high initial supersaturation. In the case illustrated, this is due to a reduction in the growth rate of crystals initially grown at a high supersaturation; the crystals initially grown at low supersaturation (1.50 and 2.20%) did not have significant increases in growth during the second period of growth. This is illustrated in Figure 9, where the growth rate function is plotted for crystals initially grown at 1.5% supersaturation and 5.0% supersaturation. It is important to note that although the differences in growth rates for the crystals with growth histories at high and low levels of supersaturation is often within the 90% confidence intervals on the determinations, the crystals with a growth history at low supersaturation always have a higher measured growth rate than those with a growth history at high supersaturation.

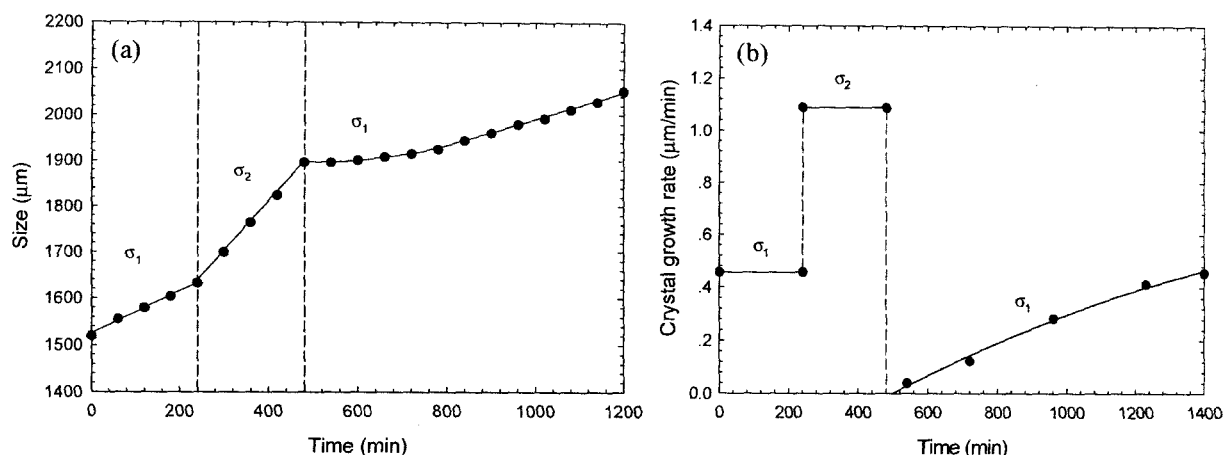


Figure 10. Crystal growth behavior of sucrose under varying conditions of supersaturation: (a) crystal size vs time; (b) crystal growth rate vs time.

The effect of growth history was further studied (in the pipe-cell crystallizer) by initiating sudden step changes in supersaturation in which the initial growth was at a low supersaturation, followed by a period at high supersaturation, and then returning to the initial supersaturation for a longer period of time. As illustrated in Figure 10a, the size of the crystal increases linearly with time during the initial periods of growth, indicating constant crystal growth. When crystals are returned to a solution of low supersaturation, the growth of the crystal does not follow the typical behavior of constant growth rate under constant supersaturation. The growth rate just after the supersaturation change is essentially zero but increases with time and approaches a constant growth rate as the crystal heals. As a result, the growth rate is lower than during the initial period of growth at the same supersaturation. However, the new period of slow growth tends to heal the surface of the crystal, and eventually (typically after more than 5 h of growth) the crystal growth rate returns to what it was in the initial period of growth. This is demonstrated in a plot of the crystal growth rate with respect to time in Figure 10b.

Experiments were also performed with two sets of supersaturation jumps, having variable growth times at each level of supersaturation (1, 2, and 3 h of growth), to determine if low growth rates can enhance crystal growth rates past normal growth kinetics and investigate the effect of healing time on subsequent crystal growth. Replicate experiments were performed for each condition. Example results from these experiments are given in Figure 11. It is interesting to note that the effect of the growth conditions is not symmetric. The crystals grown at low supersaturation initially do not have any unusual behavior when subsequently grown at higher supersaturation for short periods of time, while crystals initially grown at high supersaturation have a pronounced reduction in growth when subsequently added to lower concentration syrups.

These experiments demonstrate that growth at high supersaturation has the effect of decreasing subsequent crystal growth rates. Periods of growth at low supersaturation may heal the crystal, thus allowing the crystal to regain normal growth kinetics but cannot

improve the growth rate beyond this point; once the surface has been repaired by a period of slow growth, the growth rate is not further enhanced. The time required for healing is of the order of several hours of growth. It is also interesting that the thickness of the crystal layer required to heal the surface (which can be calculated from the growth rate and healing time) is in excess of 100 μm . This is far greater than the magnitude of the surface roughness, which is of the order of 10 μm . This suggests that a significant amount of good quality crystal lattice is required at the surface of the crystal for the crystals to grow at their normal rate. The experiments in the current study were performed only with large crystals, so it is difficult to conclude whether a similar increase in size would be required to repair very small crystals. The authors believe that a smaller increase in crystal dimension may allow the repair of the surface of crystals smaller than 100 μm .

The population of crystals used in the experiments has a distribution of growth rates (instead of a uniform growth rate across the population) before the experiment commences and still has a distribution of growth rates after the series of supersaturation steps. If the healing time at low supersaturation is sufficient, the distribution of growth rates during the final period is very similar to the distribution of growth rates at the beginning of the experiment. This does not suggest that each crystal has the same growth rate before surface degradation and after healing; however, these two growth rates will be similar, with the latter growth rate either slightly greater or less than the growth before the surface is damaged.

The hypothesized cause of the effects discussed in the previous sections is that at relatively high supersaturation the concentration of solute molecules in the adsorbed layer is sufficiently high as to have a negative effect on the surface integration of solute molecules. Common models of surface integration assume either a reasonably orderly surface migration of individual solute molecules to integration sites (BCF and similar models) or surface nucleation of small sized islands followed by growth of the islands. More recent advances in surface migration using scanning tunneling microscopy (STM) have shown that very large clusters, of

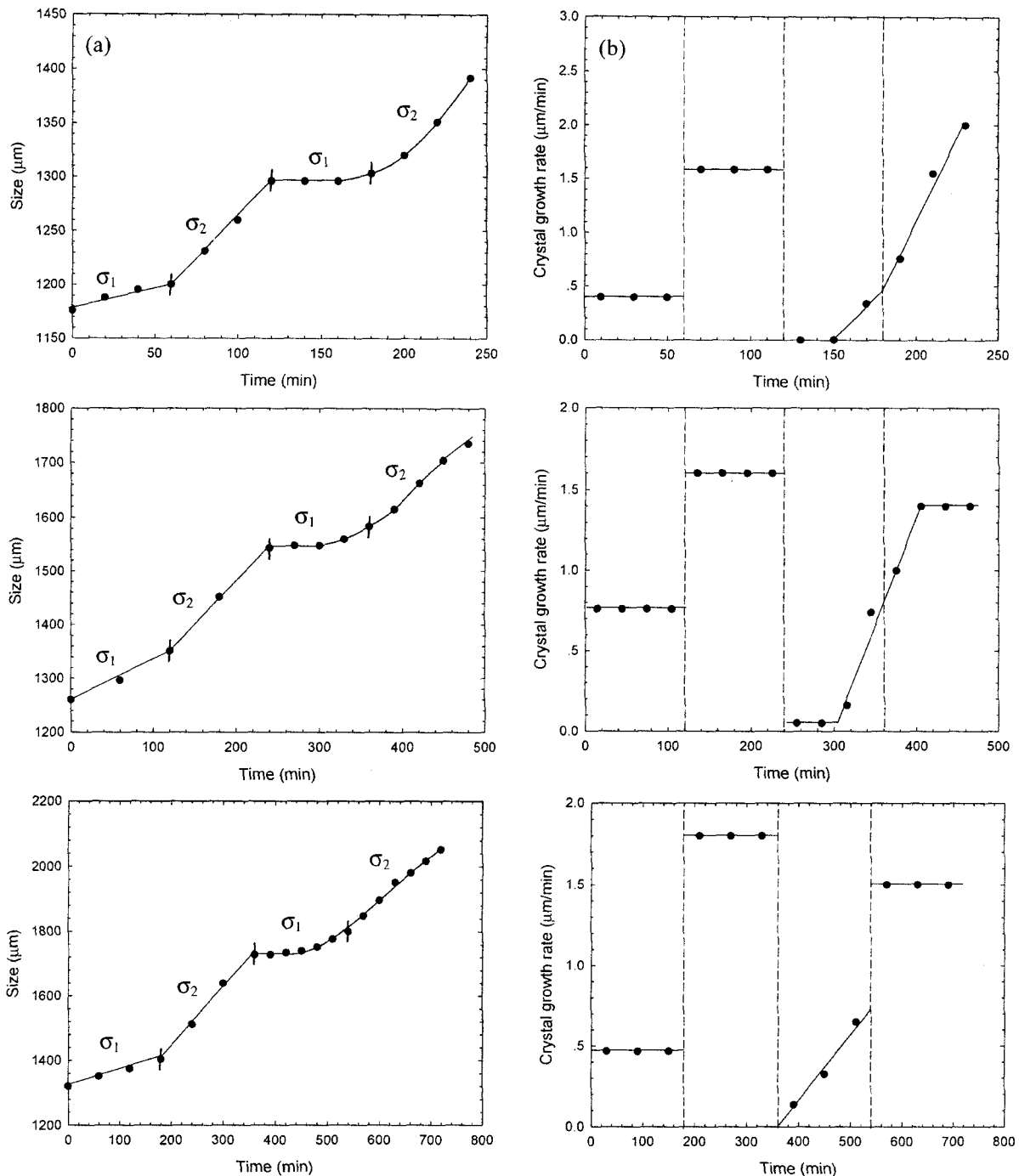


Figure 11. Healing period of sucrose crystals demonstrated by three jumps in relative supersaturation. (a) Crystal size vs time and (b) crystal growth kinetics during the healing period.

greater than 100 units, may display random migration on a surface.⁹ These clusters are not 1-D but also have significant size perpendicular to the surface. If the clusters become sufficiently large that their energy is comparable to the bulk crystal, there may be a solidification of the cluster onto the surface of the crystal that does not align perfectly with the underlying crystal lattice. The SEM results from crystals grown at high supersaturation show a very rough surface being cre-

ated from a surface that was initially very smooth: this transition is difficult to explain using models assuming addition of individual growth units to the crystal but can be understood if imperfect integration of clusters or large surface nuclei is assumed. The imperfections in the crystal lattice at the surface of the crystal would cause pinning of crystal growth at the intersections of the two lattices, a concept that is illustrated in Figure 12. The mechanism is most significant at high super-

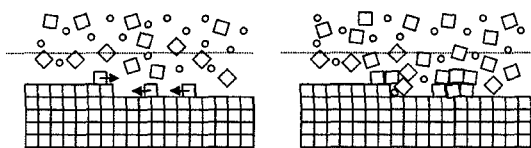


Figure 12. Hypothesized effect of high supersaturation growth on surface growth perfection. (Left) Slow crystal growth leading to smooth surfaced crystals with near-ideal lattice and (right) fast growth resulting in surface lattice imperfections due to incorrect integration of clusters.

saturation, where clusters are likely to be larger, and at fast growth rates, where imperfections are less likely to be able to reform into good lattice.

Another possible mechanism for the behavior seen in the current study is that changes in the solution structure very close to the surface of the growing crystal when the supersaturation is changed rapidly might contribute to unusual growth kinetics in the early periods of the new crystal growth. The authors believe that this cannot fully explain the current situation, where clear correlations between surface roughness and growth rate can be noticed. The very long time periods required for healing also suggest this may be an effect from the solid phase, which has low kinetic rates, rather than in the liquid phase where changes may occur more rapidly.

The proposed mechanism predicts that periods of fast crystal growth result in lower average growth rates during later periods and would also produce an imperfect crystal lattice; this may relate to previous research that related high values of the mosaic spread to low crystal growth rates. It is also interesting to compare this to the work of Jones and Larson¹⁰ who found that, in some cases, nuclei produced at high supersaturation grew slower than other nuclei when added to the same solution. It is possible that the inhibition is not fully determined in the nucleation step but is influenced by the early growth of the nuclei.

Conclusions

The rate of crystal growth of sucrose appears to be determined by the relative supersaturation of the solution the crystals are grown from and the growth rate history of the crystal. Solutions of low supersaturation produce smooth faceted crystals apparently from an

ordered integration of solute molecules, while solutions of higher supersaturation produced rough surfaced crystals apparently due to imperfect integration of clusters of solute molecules at higher rates of growth. When grown in the same solution, crystals previously grown at high supersaturation tend to have lower growth rates than those previously grown at lower supersaturation. This is believed to be due to the imperfect crystal lattice available at the surface of the crystal if the crystal previously had relatively high rates of growth; the effect may be reversed (smoother surfaces and higher growth rates) if the surface of the crystal is healed by growth at low supersaturation. The healing process is potentially very slow, requiring up to 10 h of growth.

It is believed that the imperfect integration of solute molecules during fast growth may produce pinning sites, which inhibit further integration of solute molecules. A significant period of growth at lower supersaturation allows the surface to be renewed with orderly layers of solute molecules covering the previously imperfect surface. Further work is in progress to verify the mechanism suggested in this study using atomic force microscopic studies of crystal growth of inorganic species.

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