Role of Surface Fines on Growth Rate of L-SCMC Crystals in DL-SCMC Aqueous Solution

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Many investigators have studied crystal-growth mechanisms (Myerson, 1992; Randolph and Larson, 1988; Van Der Eerden, 1993). In most of these studies, only molecular level growth mechanisms $G_{\text{molecular}}$ were considered under ideal conditions, such as the Barton-Cabrera-Frank (BCF) model and birth and spread (B&S) model. In the context of industrial crystallizers, we should also consider macroscopic growth mechanisms (G_{macro}), because crystals are grown at higher supersaturations for higher productivity. The macroscopic (observable) surface roughness is due to crystal-crystal contact, agglomeration, and so on. So growth mechanism occurring in industrial crystallizer (G_{IC}) can be represented as

$$G_{IC} = \text{func}\,(G_{\text{molecular}}, G_{\text{macro}}) \qquad (1)$$

In the previous study, we found interesting phenomena occurring in industrial crystallizers: (1) Fines suspended in the crystallizers often stick to the surface of growing crystals (Toyokura et al., 1984, 1989; Yokota and Toyokura, 1992); (2) These fines were found to increase the crystal-growth rate (Toyokura et al., 1984, 1989; Yokota and Toyokura, 1992). These results suggest that fines play an important role by affecting G_{IC} and/or quality of product crystals. However, in regard to the mechanisms, it is unknown how and/or why do the suspended fines stick to the surface of a growing crystal and how do the surface fines affect the crystal growth rate.

In this investigation an attempt is made to elucidate these mechanisms. s-carboxymethyl-L-cysteine (L-SCMC) crystals with originally clean surface were grown in DL-SCMC solution in the presence of suspended fines generated in a separate vessel. The change of the surface states (formation of surface fines) was observed under an optical microscope. Comparative growth tests were also performed in clear (in the absence of suspended fines) solution. In these tests, we observed the following results: (1) Some surface fines formed on the originally clean surface even in clear solution; however, the originally clean surface grew more rapidly and most of the fines buried. Apparently, no additional fines were observed on the new clean surface; (2) The secondary nuclei were able to stick to the surface when the fractional coverage by surface fines reached nearly 40% (area ratio). When the fractional coverage was less than 40%, suspended fines seldom stuck on the surface; (3) The fraction of the surface of a growing crystal that is covered with surface fines correlated very well with the growth rate of individual crystal face.

Experimental Procedure

The experimental setup consists of feed tank (35 L), circulation pump, filter (cellulose nitrate, pore size = 0.45 μm), flow meter, heat exchanger, nucleator, observation cell, and dissolution tank (10 L) (Figure 1a). L-SCMC crystals used for growth experiment were slowly (about 1 week) prepared in the stagnant solution of L-SCMC. They have macroscopically clean surface and are about 2 to 4 mm in length. They had typically different three faces (a-, b-, c-faces) (Figure 1b). In order to observe the surface state and the size of three different faces in a cell, two crystals fixed at the top parts of stainless wires using epoxy adhesive were set in the growth cell. The top view of the growth cell is shown in Figure 2b. Size in L_a and surface states of b- and c-faces can be seen by the state in lefthand side of Figure 2b. Other ones (L_b, L_c and a-face) can be seen by rotating the stainless wire by 90 degrees.

Sodium chloride doped (Yokota and Toyokura, 1990) aqueous solution of DL-SCMC of a desired composition was stored in a feed tank and the dissolution tank. The solution from the feed tank passed through the heat exchanger, where the solution was supersaturated by cooling, and it was continuously fed into the observation cell while L-SCMC crystals were grown. The surface states of the L-SCMC crystals were observed through an optical microscope. Sizes of the crystals (L_a, L_b, L_c) were measured every 15 to 30 min. During this operation, a number of the surface fines were also counted by the same frequency for observation of crystal size.

In some tests, some fines caused by a secondary nucleation mechanism were prepared in a separate vessel (nucleator) and the L-SCMC crystals were grown in the presence of suspended fines. The results were compared with those in clear solution.

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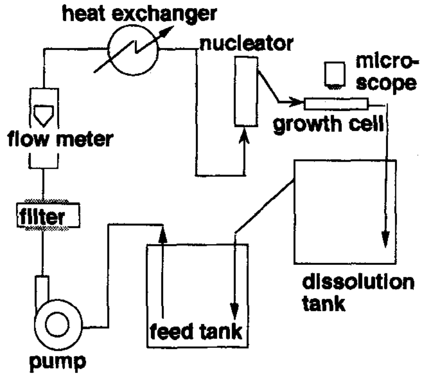
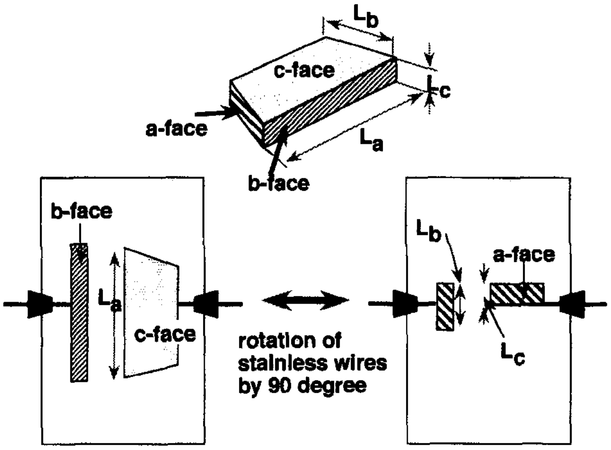


(a) Experimental set-up



(b) Definition of individual faces and observation method of them.

Figure 1. Experimental setup.

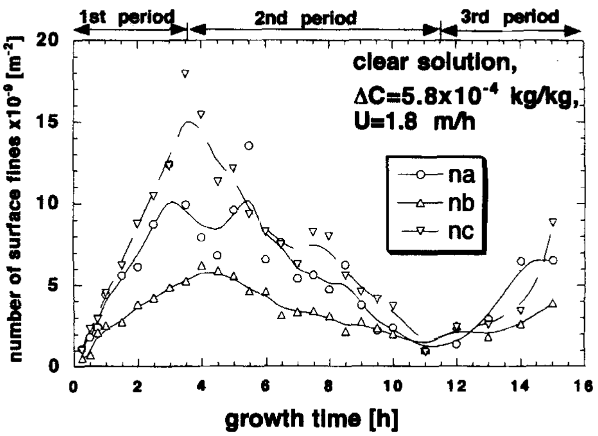
(a) Definition of individual faces of a L-SCMC crystal; (b) observation method.

Operational variables are operational supersaturation (ΔC) and flow rate of solution in the growth cell (U) ($5.8\times10^{-4} < \Delta C < 15.7\times10^{-4}$ kg solute/kg solution, $1.8 < U < 18.1$ m/h).

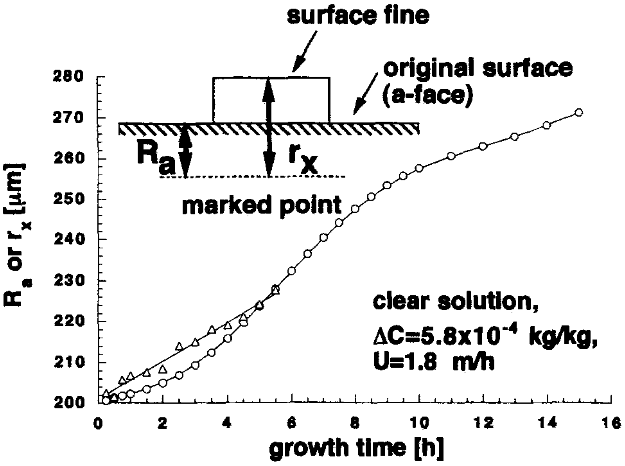
Results and Discussion

Formation of surface fines

Some fines appeared on the original clean surface (surface fines) even in the clear solution. Initially observed, their sizes were about a few micrometers. We suggest the origin of the surface fines is surface nuclei formed and/or small crystalline particles of nonobservable size (far less than a micrometer) stuck on the surface. They grew to observable size range by growth and by a combination among them. Transient numbers of the surface fines observed on individual faces (a-, b-, and c-faces) (see Figure 2b) were plotted in Figure 2a ($\Delta C = 5.8\times10^{-4}$ kg solute/kg solution; $U = 1.8$ m/h). We can see from these plots that the number of surface fines appearing on individual surfaces (n_a, n_b, and n_c) increased linearly in the initial four hours (1st period). The rate of the increase was different for each surface. We believe this may have come from the different chemical structure of each surface (we have not checked it). After the 1st period, most of the fines became buried because the originally clean surface grew more rapidly and apparently additional fines on the new clean surface were not observed (2nd period). On longer periods of growth, some surface fines reappeared on the new clean surface (3rd period). This is a very interesting phenomenon. In order to understand this fact, we devised measurement as shown in Figure 2b; that is, we measure two kinds of distances. One is the distance between the fixed point (marked by ink or crack which originally appeared) and original surface (R_a), and the other is that between the fixed point and top surface of a surface fine (r_x). Transient measurement of R_a and r_x gave us growth rates in vertical direction of the original surface and top surface of the fine, respectively. Figure 2b shows a typical example observed in clear solution. r_x increased almost linearly with the time. On the other hand, interestingly, R_a has s-curved plots. It seems that surface fines affect the growth rate of original surface, and the degree of effect is dependent on the physical (arrangement) or chemical (bonding) affinity. From these results, we can explain the characteristic behavior of surface fines. For the first period, the growth rate of the top surface of the fines (dr_x/dt) is



(a) Transient number of surface fines



(b) R_a, r_x versus time

Figure 2. Transient number of surface fines observed on the L-SCMC crystals grown in clear solution (a); R_a, r_x vs. time (b).

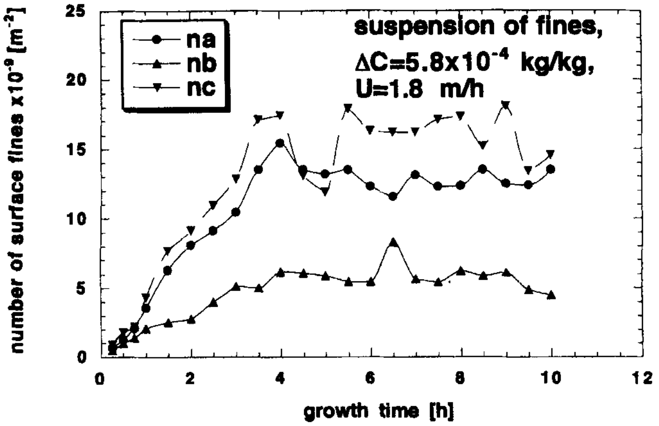


Figure 3. Transient number of surface fines observed on the L-SCMC crystals grown in suspensions of fines.

larger than that of the original surface (dR_a/dt) and the newly formed surface fines grow to observable size during this period. After this, the situation changed. dR_a/dt became larger than dr_x/dt. Eventually, the surface fines became buried at about 6 h. From 6 to 12 h, we can observe the maximum growth rates of original surface. Apparently during this period, newly formed crystalline particles did not grow to observable size because they became buried immediately after their formation. After 12 h, the dR_a/dt decreased gradually. The surface fines are suggested to be able to grow to observable size again. The effect of crystallographic factors have not been considered because of the paucity of such information. We need further experiments to discuss this approach.

In other test runs carried in clear solutions, we observed the same kind of upward curvature similar to that in Figure 2a. The time at which the maximum number of surface fines observed was strongly dependent on the operational supersaturation, but the effect of flow rate of the solution was negligible.

Figure 3 presents an example of transient numbers of surface fines observed in the presence of suspended fines ($\Delta C = 5.8 \times 10^{-4}$ kg-solute/kg-solution; $U = 1.8$ m/h). The number of surface fines observed in 1st period (initial four hours) is almost the same as that for clear solution (Figure 2a). In this period, suspended fines formed in the separate vessel seldom stuck on the surface. The remarkable difference between clear solution and solution with suspended fines was seen in the 2nd and 3rd periods. In these periods, the suspended fines were observed to stick to the surface and the number of surface fines did not decrease but remained at constant level. It is likely that the suspended fines stick to the surfaces of growing crystals when the surface becomes rough (rough means macroscopic roughness caused by formation of surface fines). To evaluate this quantitatively, we introduced a roughness index; that is, the fraction of the surfaces of a growing crystal that is covered with surface fines (fractional coverage, ϵ) defined as

$$\epsilon = S_f / S_o \tag{2}$$

Here, S_f is the surface area of a growing crystal that is covered with surface fines, and S_o is the area of the original surface of a growing crystal (include S_f). The fractional coverage during 1st period increased with time, but the fraction did not exceed 40%. During 2nd and 3rd periods, the fraction was maintained at an approximately constant level (40%). Interestingly, the suspended fines were able to stick on the surface of the growing crystal when the fractional coverage was approximately 40% independent of supersaturation and flow rate of the solution. We conclude that the tendency of stickiness of suspended fines could be influenced by amount of the surface fines.

Fluctuation of face growth rates and roll of surface fines on growth rate

Typical examples of growth rates of individual crystal faces grown in clear solution and in suspension of fines are shown in Figures 4a and 4b, respectively ($\Delta C = 5.8 \times 10^{-4}$ kg solute/kg solution, $U = 1.8$ m/h). In both cases, the growth rates fluctuated during each run (solution concentration change during the run was within 1.0×10^{-6} kg SCMC/kg solution). So, the change in solution concentration seems to be less effective, and the shape of the curves was similar to those of transient number of surface fines (see Figures 2a and 3), qualitatively. The time at which maximum growth rates were achieved (in Figure 4a) was shifted to the right as compared to the time at which the maximum number of surface fines was observed (in Figure 2a). On other test runs, the same

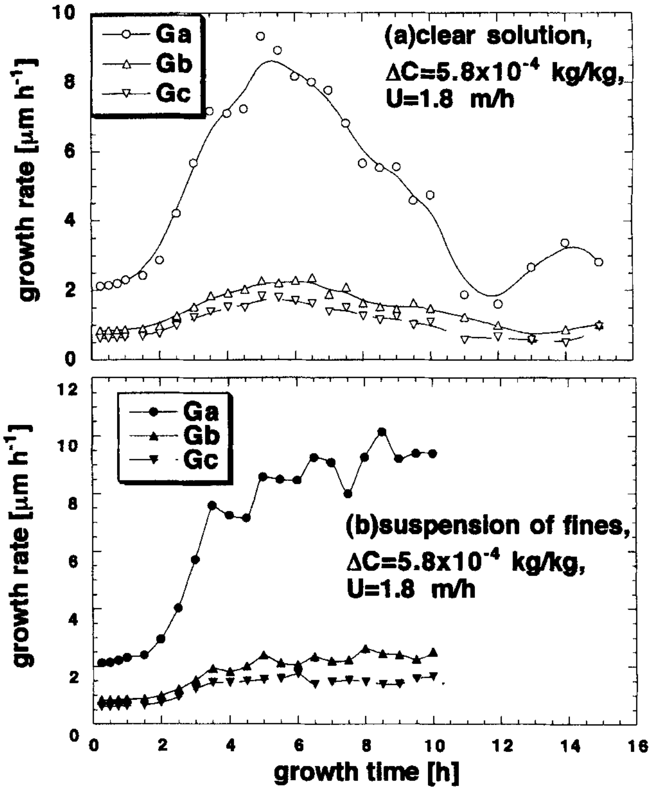


Figure 4. Transient growth rates of the L-SCMC crystals grown in (a) clear solution and in (b) suspension of fines.

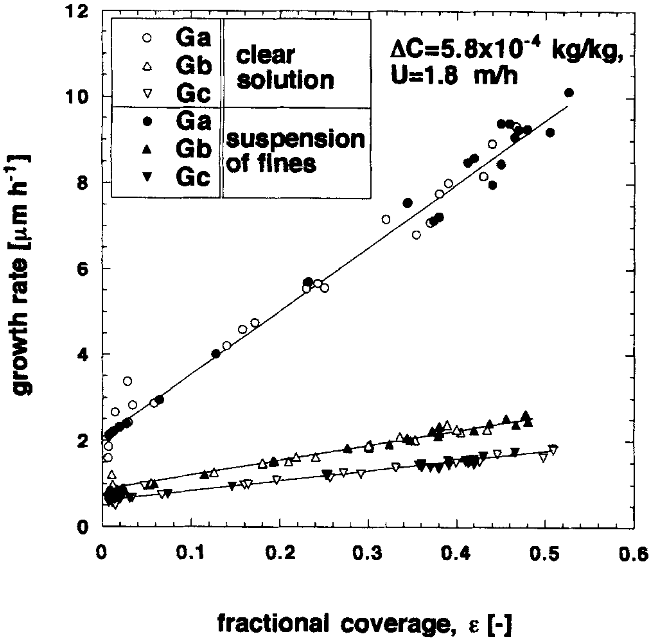


Figure 5. Examples of relations between growth rates and fractional coverages.

curved plots were obtained and the time of maximum growth rate decreased with increase of operational supersaturation. In the case of the test in the suspension of fines, G_a, G_b, G_c increased (Figure 4b) in the same way as with Figure 4a for an initial period. However, after these periods G_a, G_b, G_c remained constant. We believe this is due to the roughness of the surface. The growth rates were plotted against fractional coverage, as shown in Figure 5. From this result, G_a, G_b, G_c were correlated with fractional coverage. The regression coefficient is nearly unity indicating the degree of excellent fit. The following relations are obtained:

$$G_a = G_{a0} + k_a \epsilon_a \tag{3}$$

$$G_b = G_{b0} + k_b \epsilon_b \tag{4}$$

$$G_c = G_{c0} + k_c \epsilon_c \tag{5}$$

In these equations, G_{a0}, G_{b0}, G_{c0} are the intercepts in Figure 5 and may indicate the molecular level growth rate because fractional coverages are zero. G_{a0}, G_{b0}, G_{c0} were correlated with operational supersaturation, as shown in Figure 6a.

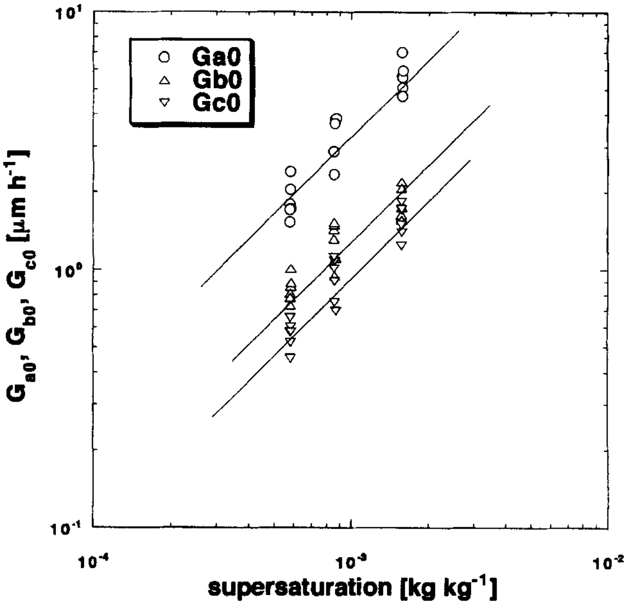
$$G_{a0} = 4.1 \times 10^3 \, \Delta C \tag{6}$$

$$G_{b0} = 1.3 \times 10^3 \, \Delta C \tag{7}$$

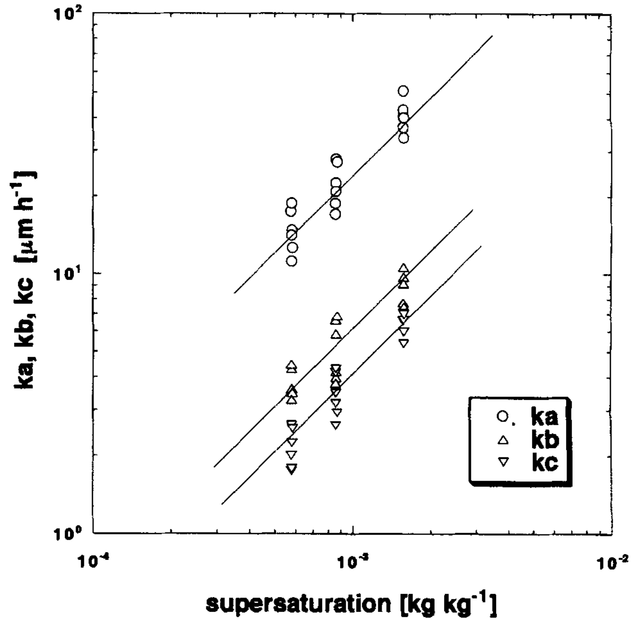
$$G_{c0} = 0.9 \times 10^3 \, \Delta C \tag{8}$$

Unknown parameters are the constants k_a, k_b, k_c (slope of the lines in Figure 5). Although we do not know their physical meaning, k_a, k_b, k_c were correlated with operational supersaturation independent from the solution flow as

$$k_a = 2.9 \times 10^4 \, \Delta C \tag{9}$$



(a) G_0 versus ΔC



(b) k versus ΔC

Figure 6. (a) G_0 vs. ΔC; (b) k vs. ΔC.

$$k_b = 5.9 \times 10^3 \, \Delta C \tag{10}$$

$$k_c = 3.5 \times 10^3 \, \Delta C \tag{11}$$

When crystal growth kinetics occurring in industrial crystallizers are considered, the surface fines could play a significant role as shown in this study. For the design and optimal operating conditions for the production of high quality crystals, the control of the surface fines and/or suspended fines could be a key factor.

Notation

ΔC = operational supersaturation, kg solute/kg water
G_a, G_b, G_c = growth rate of L-SCMC crystal, μm/h
G_{a0}, G_{b0}, G_{c0} = growth rate of a L-SCMC crystal of zero fractional coverage, μm/h
k_a, k_b, k_c = constants in Eqs. 3–5
L_a = length of a L-SCMC crystal, μm
L_b = width of a L-SCMC crystal, μm
L_c = depth of a L-SCMC crystal, μm
n_a, n_b, n_c = number of fines appearing in unit surface area of L-SCMC crystals, 1/m^2
R_a, r_x = distances defined in Figure 2a, μm
U = flow rate of a solution in the growth cell, m/h

Greek letters

ϵ = fractional coverage

Subscripts

a = a-face
b = b-face
c = c-face

Literature Cited

Myerson, A. S., and R. Ginde, *Handbook of Industrial Crystallization*, A. S. Myerson, ed., Butterworth-Heinemann, Boston, p. 52 (1992).

Randolph, A. D., and M. A. Larson, *Theory of Particulate Processes*, 2nd ed., Academic Press, San Diego, p. 117 (1988).

Toyokura, K., T. Kikucki, and Y. Aoyama, "Behavior of Fines in Supersaturated Solution," in *Industrial Crystallization 84*, S. J. Jancic and E. J. de Jong, eds., Elsevier Science, Amsterdam, p. 37 (1984).

Toyokura, K., H. Sakai, and R. Uchida, "Effect of Suspended Fines on the Crystal Growth," in *Industrial Crystallization 87*, J. Nyvlt and S. Zacek, eds., Elsevier, Prague, p. 215 (1989).

Yokota, M., and K. Toyokura, "The Growth of L-SCMC Crystal and Its Optical Resolution," *J. Crystal Growth*, **99**, 1112 (1989).

Yokota, M., and K. Toyokura, "Heterogeneous Nucleation of D-SCMC on the Surface of L-SCMC Crystals," AIChE Extended Abstract, p. 739 (1992).

Van Der Eerden, J. P., *Handbook of Crystal Growth*, D. T. J. Hurle, ed., Elsevier Science, North-Holland, p. 311 (1993).

Manuscript received Apr. 25, 1994, and revision received Feb. 6, 1995.