Formation of Regularly Arrayed Fines on Surface of Sodium Chloride Crystals

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We observed regularly arrayed fines (RAFs) (Figure 1) on the surface of sodium chloride crystals produced from both commercial-scale (Nakamura et al., 1990) and laboratory-scale (Nakano, 1991) crystallizers. Purity of the crystals might be lowered by RAFs, with which mother liquor is included. Therefore, control of RAFs is very important for the manufacture of sodium chloride crystals.

Although crystallization of sodium chloride has been studied by many investigators, only a few have paid attention to RAFs. Nakano (1991) and Kubota et al. (1993) tried to explain the formation of RAFs by either of two mechanisms: the adhesion of suspended fines and surface nucleation. Unfortunately, due to lack of experimental evidence, they were not able to formulate a conclusion concerning RAFs formation mechanism.

We first review previous studies on sodium chloride crystallization. Some of them are summarized in Table 1. Table 1 reveals an interesting tendency concerning the formation of RAFs. Only Matsuoka et al. (1993) used recrystallized seed crystals. Their seed crystals grew with smooth surfaces and RAFs could not be seen. Other investigators have used commercially produced crystals without any pretreatment, and in these cases RAFs could be seen. This suggests that seed quality is an important factor influencing the formation of RAFs. In this study, we prepared two kinds of seed crystals: recrystallized seeds (seed A) and commercially produced crystals (seed B). We examined the effect of seed quality on the formation of RAFs. We present an experimental evidence which shows how RAFs form and grow by an *ex-situ* observation method using scanning electron microscopy (SEM).

Experimental Studies

Preparation of seed crystals

Seed A (Recrystallized Seed Crystals). Seed A was naturally grown crystals and prepared as follows. Prescribed amounts of reagent grade sodium chloride crystals (Kanto Chemical Co., Inc.) were dissolved in distilled water, and the solution saturated at about 313 K was naturally cooled to room temperature in a dish. Fines which were formed in the dish were grown for about three days. Resulting well-defined crystals (about 2–3 mm in size) were selected and used for growth experiments.

Seed B (Commercially Produced Seed Crystals). Commercial reagent grade sodium chloride crystals were gently sieved (1.5–3 mm in size) and used as seeds.

Growth experiments

Figure 2 shows an illustration of the experimental apparatus used for the growth experiments. The experimental apparatus is composed mainly of feed tank (2), feeding pump (4), heat exchanger (6) and growth cell (7). Details of the growth cell (7) are shown in Figure 3. It was made from glass tube and has a strainer in the middle. A seed crystal fixed onto a

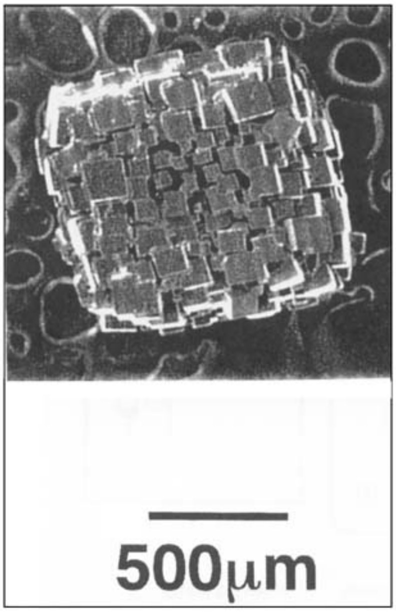

Figure 1. RAFs on a seed crystal of sodium chloride (Nakano, 1991).

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Table 1. Data on Growth of NaCl Crystals

Investigators	Apparatus	Growth Conditions	Seed Crystals	RAF
Matsuoka (1993)	Agitated vessel (batch)	Fixed crystal $T_G = 303 \sim 323$ K $\Delta T = 2 \sim 7$ K $N = 0 \sim 25$ Hz	Recrystallized	absence
Toyokura (1991)	CMSMPR	Multicrystals $T_G = 343$ K $N = 400 \sim 500$ rpm	Commercial	presence
	Fluidized bed (continuous)	Multicrystals $T_G = 343$ K $U = 2.0 \sim 5.2\ \mathrm{cm \cdot s^{-1}}$	Commercial	presence
Nakano (1991)	Fluidized bed	Multicrystals $T_G = 293 \sim 313$ K $\Delta T = 1 \sim 5$ K $U = 1.68\ \mathrm{l\ min^{-1}}$	Commercial	presence
Nagasawa (1991)	CMSMPR	Multicrystals $T_G = 293 \sim 313$K $\Delta T = 1 \sim 7$ K $N = 800, 1{,}200\ \mathrm{min^{-1}}$	Commercial	presence

T_G = growth temperature; ΔT = supercooling; N = impeller speed; U = flow rate of solution; RAF = regularly arrayed fines

stainless steel wire with epoxy adhesive was set into the cell as shown in Figure 3.

Aqueous solution of sodium chloride saturated at 313 K was prepared by dissolving a prescribed amount of reagent grade sodium chloride crystals (Kanto Chemical Co.). The solution was stored in the feed tank (318 K, undersaturated) and circulated by the pump. The solution was supersaturated ($\Delta T = 5$ K; $\sigma = 2.92 \times 10^{-3}$) by cooling to 308 K with the heat exchangers, and then fed into the growth cell. The seed crystal in the growth cell was allowed to grow in a clear solution. After a prescribed time of crystal growth, the seed crystal was taken out from the cell and the surface was observed with SEM (Hitachi, Model S-450). We repeated the same experiment for both seed A and seed B crystals, but changed the growth time in each experiment in order to observe the transient growth behavior of the surface of growing seed crystals with SEM.

By the way, Toyokura et al. (1983) reported that fines suspended in a solution sometimes adhere to the surface of growing seed crystals. In order to examine the effect of the adhesion of suspended fines on the formation of RAFs, a seed crystal was grown in the presence of suspended fines as

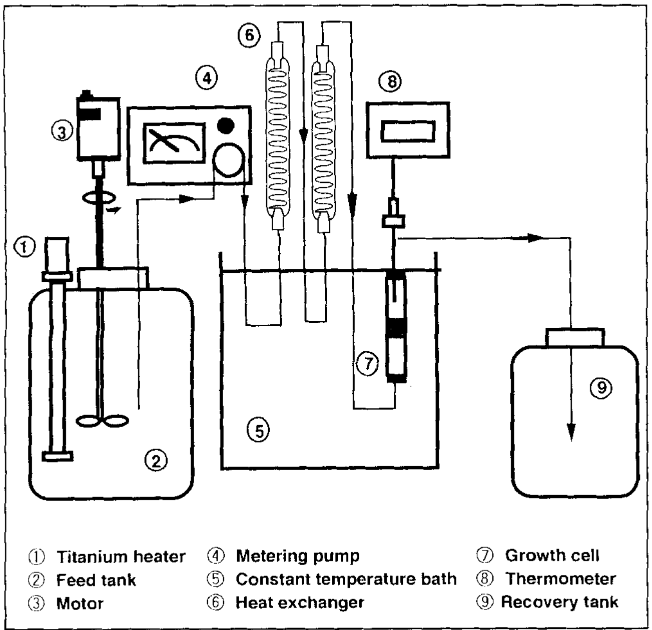


Figure 2. Experimental apparatus.

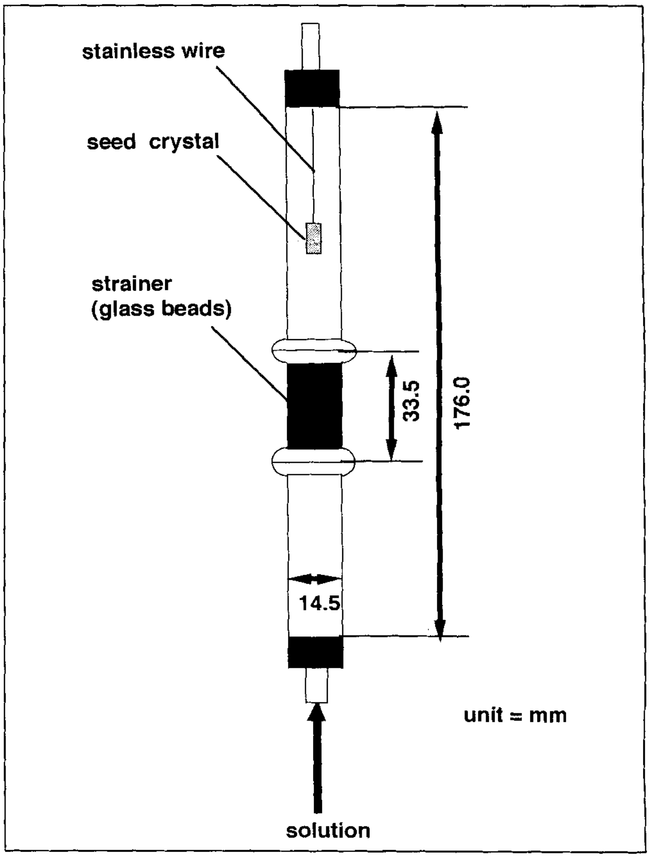


Figure 3. Dimensions of the growth cell.

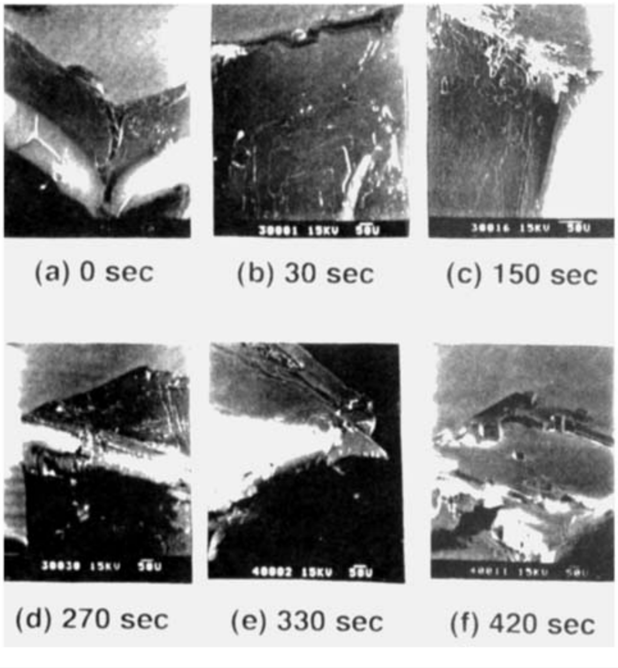
follows. In an experiment using seed A, many nuclei were produced spontaneously and they were grown to form a fluidized bed of sodium chloride crystals at the bottom of the cell. From the bed, new nuclei were generated by secondary nucleation mechanism, and were made to pass through the seed crystal to grow it in the presence of suspended fines.

It is well-known that crystalline dust is sometimes generated on evaporation of the adhering solution. We must avoid this problem in the discussion of the surface topography. We checked this problem using a seed A crystal. The seed A is appropriate for this purpose, as it has an originally smooth surface. The seed A crystal was observed with SEM with no treatment (sample 1). The other two seeds (seed A) were immersed in a saturated solution of sodium chloride of saturation temperature of 313 K. After about one min, one crystal was removed and was used as a SEM sample (sample 2). By lowering the temperature, the other immersed crystal was grown for about 10 min in a clear solution ($\Delta T = 5$ K; $\sigma = 2.92 \times 10^{-3}$) (sample 3). The surface topography of samples 2 and 3 were similar to the original surface (sample 1) and crystalline dust was hardly seen even after ten min growth (sample 3). These results show that there is a negligible effect of crystalline dust, produced on driving, on the surface topography of growing crystals.

Results and Discussion

Effect of seed quality on formation of RAF

Figure 4 shows photographs of time sequence of seed A grown in the clear solution. It is difficult to compare each picture quantitatively, as each picture was taken for different crystals. However, general qualitative tendency in the formation of RAFs and the development of macroscopic surface roughness can be discussed. The seed A has an originally smooth surface (Figure 4a), and the smooth surface was virtually maintained even after 30 to 420 s of growth. Sometimes, macrosteps and a few fines (Figures 4b–4f) appeared. RAFs could not be seen at all.



(a) 0 sec (b) 30 sec (c) 150 sec

(d) 270 sec (e) 330 sec (f) 420 sec

Figure 4. SEM photographs of time sequence of sodium chloride crystals grown in a clear solution (recrystallized seed crystals (seed A).
$T_G = 308$ K; $\Delta T = 5$ K; $U = 153.6$ cm·h^{-1}).

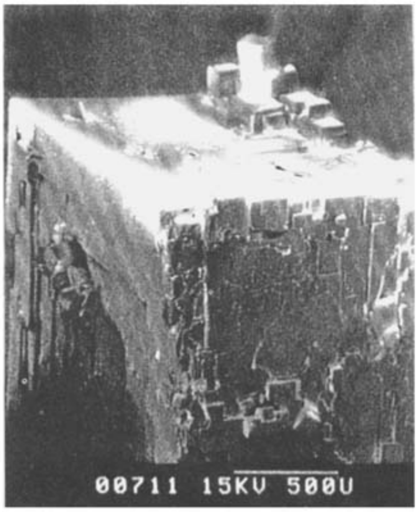


Figure 5. SEM photograph of sodium chloride crystals grown in the presence of suspended fines for 30 min (recrystallized seed crystals (seed A)).
$T_G = 308$ K; $\Delta T = 5$ K; $U = 153.6$ cm·h^{-1}).

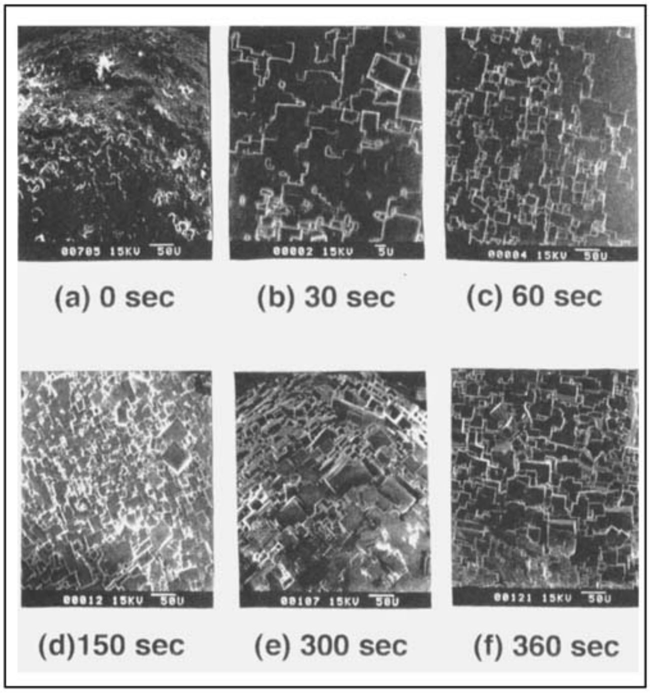
When we grew a recrystallized seed in the presence of suspended fines produced from the fluidized bed, surface fines were observed more frequently (Figure 5). The surface fines, however, were much different from RAFs. Most of the fines were formed in the corner of the seed crystal in this case.

Figure 6 shows SEM photographs of time sequence of commercially produced crystals (seed B) grown in the clear solution. As can be seen in Figure 6a, seed B has an originally rough surface. Surprisingly, the formation of RAFs was observed after only 30 s growth (Figure 6b). Seed B could have the origin of RAFs initially. When we observed the surface of the seed B carefully, we could recognize some crystalline particles of similar size in it, about 10 to 20 μm. These crystalline particles may be the origin of RAFs. They developed to well-defined RAFs during the growth of seed B as seen in Figures 6c–6f.

The questions arise here as to why only the commercially produced crystals have the origin of RAF and how are the origins of RAF generated. Here we have to remember that sodium chloride crystals are manufactured in industry in a multicrystal system. What happens in industrial crystallizers? In order to investigate this, we observed the growth behavior of multicrystals in an agitated vessel.

Growth behavior of multicrystals in an agitated vessel

The experimental procedure here was very simple. We carried out batch crystallization using a 500 mL agitated vessel. A solution saturated at 313 K was agitated in the vessel at 318 K (undersaturated), and then, cooled naturally to room temperature. About one to two hours after cooling, fines were



(a) 0 sec (b) 30 sec (c) 60 sec

(d)150 sec (e) 300 sec (f) 360 sec

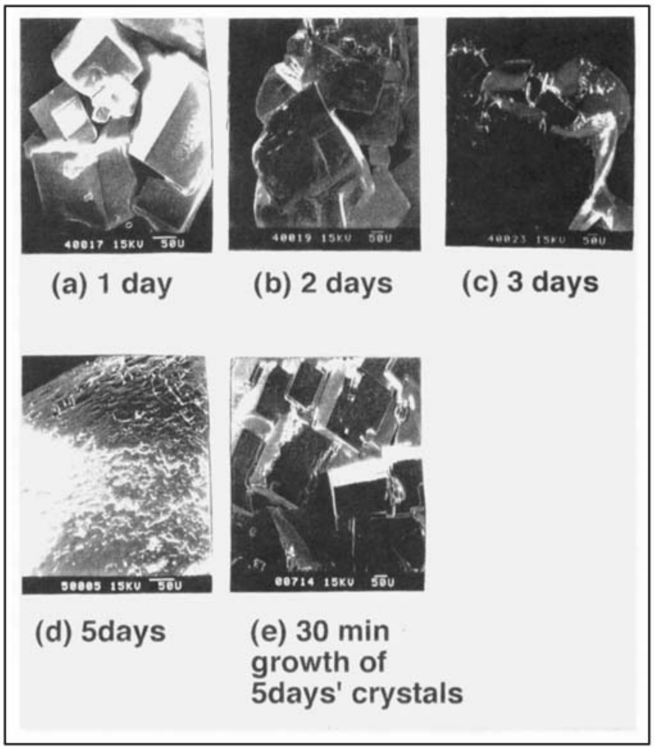
Figure 6. SEM photographs of time sequence of sodium chloride crystals grown in a clear solution (commercial seed crystals (seed B)).
$T_G = 308$ K; $\Delta T = 5$ K; $U = 153.6$ cm·h^{-1}).

formed by the primary nucleation mechanism. The fines were allowed to grow in the solution and secondary nucleation was allowed to occur. In time, the solution reached a saturation state. The crystal suspension was agitated at room temperature for an additional five days. During this, crystals were sampled from the solution everyday, and the surface of them was observed with a SEM.

Figure 7 shows SEM photographs of time sequence of grown suspended crystals. On the first day, almost all of the crystals were agglomerated (Figure 7a), but the surface of individual crystals was very smooth. The corner of the crystals became rounded by attrition and the surface gradually became rough (Figures 7b and 7c). After 5 days (Figure 7d), the surface state of crystal became similar to that of the commercial crystals (Figure 6a). The origins of RAFs can be seen in Figure 7d. A crystal of the five days agitation was grown in a clear solution ($\Delta T = 5$ K; $\sigma = 2.92 \times 10^{-3}$) for 30 min. The surface of the grown crystal is shown in Figure 7e. The existence of RAFs can clearly be seen. This suggests that the structured origins of RAFs initially exist in sodium chloride crystals and the origins are made by attrition events.

Conclusions

From the results of *ex-situ* observation of three kinds of seed crystals (commercial crystals, recrystallized crystals, and agitated crystals) the following conclusions can be made: (1) Commercial crystals originally have the origin of RAF and well-defined RAF develop during the growth of the crystals; (2) The effect of adhesion of suspended fines on the formation of RAF is minimal; (3) The origin of RAF could be generated in an agitation vessel. This result shows that formation of RAF is a phenomenon specific to a multicrystal system.



(a) 1 day (b) 2 days (c) 3 days

(d) 5days (e) 30 min growth of 5days' crystals

Figure 7. SEM photographs of time sequence of sodium chloride crystals formed in an agitated vessel (a–d), $T_m = 313$ K, N = 200 min^{-1}), and 30 min growth of 5-day-old crystals in clear solution (e), $T_G = 308$ K, $\Delta T = 5$ K, $U = 153.6$ cm·h^{-1}).

Acknowledgment

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Notation

N = impeller speed, min^{-1}
t = growth time, s or min
T_G = growth temperature, K
ΔT = supercooling, K
U = flow rate of solution, cm·min^{-1}
σ = supersaturation ratio

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