Estimation of Number of Surface Crystals on Sodium Fluoride Mother Crystal in Crystallization

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Abstract—A simple model was developed to explain the surface crystals found on the clear mother crystal face. The surface crystals on the mother crystal in the reaction crystallization of sodium were mathematically estimated by using a model based on two-dimensional secondary nucleation and two-step growth mechanisms. The model predicted that the surface crystals found on the mother crystal would be sensitive to the reactant concentration and agitation speed due to their influence on the interfacial supersaturation in the crystal growth. As the bulk supersaturation increased and the molecular transport was facilitated, the number of surface crystals on the mother crystal also increased, because the interfacial supersaturation built up on the mother crystal surface was enhanced. The prediction of the number of the surface crystals on the mother crystal appeared to be consistently comparable with experimental results.

Key words: Sodium Fluoride, Surface Crystal, Secondary Nucleation, Two-Step Growth Interfacial Supersaturation, Crystallization Conditions

INTRODUCTION

In crystallization, secondary nucleation frequently plays an important role in determining the crystal size and shape because new nuclei are generated on the crystal surface even at low supersatuartion level, resulting in the multi-dispersed size distribution and irregular shape of crystals in the suspension. Therefore, much research has focused on investigating the influence of secondary nucleation on the product suspension.

In general, there are many reasons for secondary nucleation: contact, attrition, fluid shear etc. [Change et al., 1982]. Based on the mechanism of Denk and Botsaris [1972], secondary nucleation has been described as the nuclei on the crystal surface being generated by the driving force of the concentration gradient, which originates from mass transfer around the crystal. Thus, they showed experimentally in cooling crystallization that secondary nucleation was promoted as the supercooling and agitation of the solution increased. Contact nucleation of various crystals was intensively investigated by Tai et al. [1975]. Their study considered that secondary nucleation might primarily be initiated by the impact on the crystal surface by the other crystals, impeller and reactor wall. Then, the secondary nucleation rate was suggested as a function of impact energy. A similar influence of the impact on the contact nucleation was observed by Denk and Botsaris [1972]. The importance of the impact on the secondary nucleation was mathematically developed by Ploss and Mersmann [1989] using the theory of Hertz/Huber. In the study, many factors influencing secondary nucleation were suggested as crystallizer type, impeller type, operating parameters, physical properties of solution and crystal and supersaturation and growth kinetics etc. Among them, the bulk supersaturation and mechanical stress by agitation were considered as most influencing fac-

tors on secondary nucleation. The importance of supersaturation on secondary nucleation was also explained by Tai et al. [1993].

Tai et al. [1992] developed the most instructive study on the secondary nucleation mechanism. Here, the secondary nucleation on the crystal surface was actually due the interfacial supersaturation, which meant the supersaturated concentration on/around crystal surface. Basically, the secondary nucleation on the crystal was promoted as the interfacial concentration and at a fixed interfacial supersaturation was modified by external stimuli, such as impact, contact, shear, impurity, temperature, agitation etc. In their study, the qualitative estimation of the influence of such stimuli on the secondary nucleation was based on the two-step growth mechanism [Karpinski, 1985].

It was sometimes observed in the secondary crystallization that an irregular shape of the crystal was produced [Liu et al., 1976; Denk and Botsaris, 1972]. In the crystallization of barium sulfate [Liu et al., 1976], the irregular crystal shape was characterized by small crystals growing on and with the mother crystal, which was attributed to surface crystal formation on the mother crystal due to secondary nucleation at low supersaturation. A similar surface crystal formation on the mother crystal has also been reported by Denk and Botsaris [1972] in sodium chlorate crystallization and attributed to the secondary nucleation driven by the supersaturation gradient related to the mother crystal. Likewise, in the study of sodium fluoride crystallization [Kim and Kim, 1999; 2000], an irregular crystal shape characterized by surface crystals on the mother crystal was observed. According to them, the irregular crystal shape of the sodium fluoride primarily originated from the agglomeration of the free nuclei, which was generated by the secondary nucleation. However, the possibility that the secondary nuclei remaining on the mother crystal surface grow to the surface crystal resulting in the irregular crystal shape was also suggested. Accordingly, the purpose of the present study is the model investigation of the surface crystal found on the mother crystal resulting in the irregular shape

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of the sodium fluoride crystal. A model based on the secondary nucleation process, which is interconnected with the crystal growth process, is developed to explain the surface crystal formation. The validity of the model is then examined by comparing the experimental result of Kim and Kim [2000] at various reactant concentrations and agitation speeds to change the secondary nucleation and crystal growth processes.

MATHEMATICAL DESCRIPTION

When nuclei are generated at low supersaturation, the mother crystal surface will be favored because of its low free edge energy for nucleation; that is called secondary nucleation. Some of the secondary nuclei generated on the mother crystal surface will stick to grow on the mother crystal. Those crystals growing on the mother crystal are counted as a surface crystal and can be explained on the basis of the secondary nucleation mechanism, as developed by Nielsen [1964]. According to his work, the two-dimensional nucleation rate (J') on a crystal surface can be formulated as,

$$J' \cong \frac{D}{d^4} \exp\left(-\frac{\Delta G'^*}{kT}\right) \quad (1)$$

where D is the diffusion coefficient, d is the molecular diameter, k is the Boltzmann constant, T is the absolute temperature, and $\Delta G'^*$ is the critical free energy change of a two-dimensional embryo on the crystal surface, called the secondary nucleus. The free energy change created by the formation of a secondary nucleus can be expressed as,

$$\Delta G' = -n'\varphi + L'\sigma' \quad (2)$$

where n' is the number of molecules contained in the embryo, L' is the circumference of the embryo, and σ' is the free edge energy of the embryo. The molar affinity of the phase change, φ, indicating an intensive quantity measuring the driving force of the phase change, can then be expressed as follows when the activity coefficient is assumed to be unity,

$$\varphi = kT \ln\left(\frac{C_i}{C_S}\right) \quad (3)$$

where C_i and C_S are the solute concentrations on the mother crystal surface and in the bulk solution, respectively. The ratio between the two concentrations (C_i/C_S) is usually defined as the interfacial supersaturation, S_i. At equilibrium, the critical number of molecules contained in a secondary nucleus, that is, a critical embryo, is obtained by taking a derivative of the free energy change, as follows:

$$n'^* = \frac{1}{2}\frac{\sigma'L'^*}{\varphi} \quad (4)$$

where L'^* is the circumference of the secondary nucleus. From Eqs. (2) and (4), the critical free energy change of the secondary nucleus can be rearranged as,

$$\Delta G'^* = \frac{1}{2}\frac{\sigma'L'^*}{kT} \quad (5)$$

By using Eq. (5) the secondary nucleation rate of Eq. (1) can be expressed as a function of the interfacial supersaturation as,

$$J' \cong \frac{D}{d^4} \exp\left(-\frac{\sigma'L'^*}{2k^2T^2 \ln S_i}\right) \quad (6)$$

Since it is presumed that the surface crystals appearing on the mother crystal result from the growth of secondary nuclei on the mother crystal, the number of surface crystals on the mother crystal will be predominantly determined by the secondary nucleation rate. Accordingly, the population of the surface crystals found on the mother crystal can be analogously described, similar to Eq. (6), as suggested by Tai et al. [1975] for the secondary nucleation on the mother crystal,

$$N_S \cong a_1 \exp\left(-\frac{a_2}{\ln S_i}\right) \quad (7)$$

where N_S is the number of surface crystals found on the single mother crystal and a_1 and a_2 are the proportional constants.

To predict the interfacial supersaturation on the mother crystal, a two-step growth model composed of mass transfer and surface integration steps can be adopted [Karpinski, 1985]. Under a quasi-steady state of crystal growth, the following relationship between the two steps can be derived from the model as,

$$k_c (C_b - C_i) = k_r (C_i - C_S)^r \quad (8)$$

where k_c and k_r are the mass transfer and surface integration coefficients, respectively, C_b is the bulk concentration and r is the rate order for the surface integration. In Eq. (8), the term on the left-hand side means the molecular mass transfer rate from the bulk to the interface, whereas the one on the right-hand side indicates the lattice integration rate of the molecules on the crystal surface. By introducing a dimensionless concentration, Eq. (8) can be rearranged as follows:

$$\frac{\theta_i^r}{1-\theta_i} = \alpha \quad (9)$$

where θ_i is the dimensionless interfacial concentration and α is the lump parameter, which is composed of the rate coefficients of the mass transfer and surface integration, and solubility and bulk concentration as,

$$\theta_i \equiv \frac{C_i - C_S}{C_b - C_S} = \frac{S_i - 1}{S_b - 1} \quad (10)$$

$$\alpha = \frac{R}{C_S^{r-1}(S_b - 1)^{r-1}} \quad (11)$$

$$R \equiv \frac{k_c}{k_r} \quad (12)$$

Therefore, in Eq. (9), if the surface integration order is known, the interfacial supersaturation on the crystal can be estimated by using the lump parameter, which is dependent on the crystallization conditions.

Meanwhile, according to Garside [1971], the concept of an effectiveness factor can be introduced to determine the rate-controlling step in the crystal growth process. By definition, the surface integration effectiveness factor is related to the dimensionless interfacial concentration as,

$$\eta_r = \theta_i^r \quad (13)$$

Eq. (13) indicates that as the crystal growth process becomes controlled by the surface integration step ($\eta_r \rightarrow 1$), the interfacial concentration of the crystal will approach the bulk concentration, and since the crystal growth process is determined by the mass transfer step ($\eta_r \rightarrow 0$), the interfacial concentration will be close to the solubility.

DISCUSSION

In general, the sodium fluoride crystals produced at the endpoint of the feeding in single-jet semi-batch reactor were octahedral in shape with a face-centered cubic crystal system, as displayed in Fig. 1. As demonstrated from the microscopic images even though the octahedral shape of the mother crystals was maintained regardless of the crystallization conditions, as observed by Frondel [1940] and Ring [1996], the overall configuration of the crystals, as characterized by the small crystals on the mother crystal, was found to be dependent on the crystallization conditions. The small crystals found on the mother crystal were usually counted as surface crystals generated by the secondary nucleation.

In the present model, these experimental phenomena were described by a secondary nucleation mechanism connected with the crystal growth mechanism. Normally, for crystal growth in a supersaturation condition, the solute molecules must be transported from the bulk suspension to the crystal. As a result, the interfacial supersaturation on the crystal surface is built up and then drives the lattice integration of the solute molecules on the crystal, which is called surface integration. Accordingly, the principal concept of the model to count the number of surface crystals is that secondary nucleation as well as surface integration on the mother crystal can be simultaneously induced by interfacial supersaturation. This concept of the model is conceptually consistent with that of secondary nucleation on a crystal surface as suggested by Denk and Botsaris [1972] and Tai et al. [1992]. According to the proposed model, as the interfacial supersaturation increases, the secondary nucleation is enhanced and the surface crystal formation on the mother crystal is promoted.

To predict the population of the surface crystals found on the mother crystal, the two-dimensional surface nucleation and two-step growth processes were modeled, as expressed in Eqs. (7)-(12). To solve the model equations, the surface integration order, r, was assumed as 2, as used in several previous studies on electrolyte crystals by various researchers [Nancollas, 1968; Liu et al., 1976; Nancollas et al., 1982; Gardener and Nancollas; 1983; Nielson, 1981; Nielson and Toft, 1984]. Figs. 2 and 3 show that the interfacial supersaturation varied with the coefficient ratio (R) of the mass transfer to the surface integration and bulk supersaturation (S_b). Based on the two-step crystal growth mechanism, the interfacial supersaturation of solute is determined by the mass transfer and surface integration rates because solute molecules on the crystal surface are built up by the molecular transport and spent for the lattice integration for the crystal growth. Thus, if the mass transfer is promoted
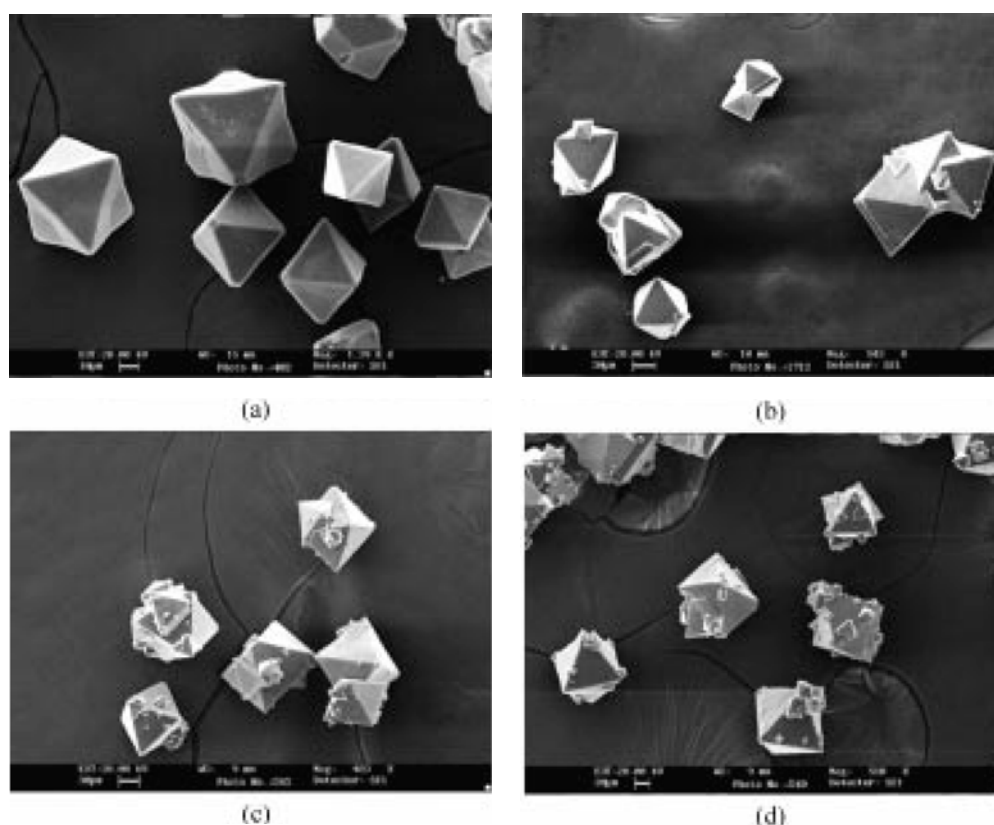

Fig. 1. Typical microscopic images of sodium fluoride crystals under various crystallization conditions in semi batch reactor.
(a) 1.75 mol/l of reactant concentration and 700 rpm of agitation speed, (b) 2.5 mol/l of reactant concentration and 1,200 rpm of agitation speed, (c) 2.5 mol/l of reactant concentration and 1,500 rpm of agitation speed, (d) 3.75 mol/l of reactant concentration and 1,500 rpm of agitation speed.
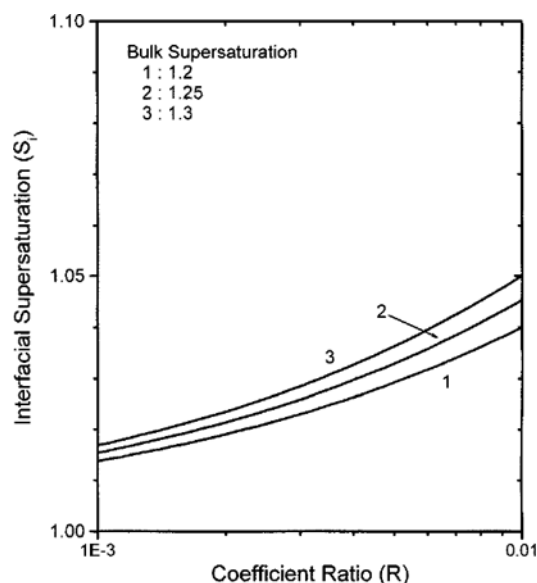
Fig. 2. Model prediction of variation in interfacial supersaturation relative to coefficient ratio between mass transfer and surface integration in crystal growth process.
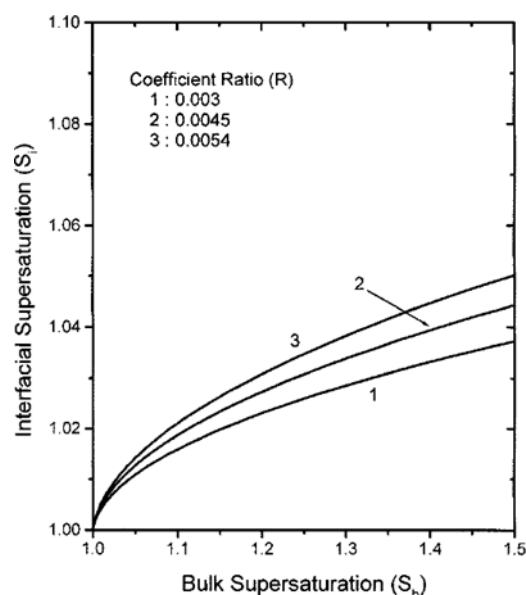

Fig. 3. Model prediction of variation in interfacial supersaturation relative to bulk supersaturation in reactor.
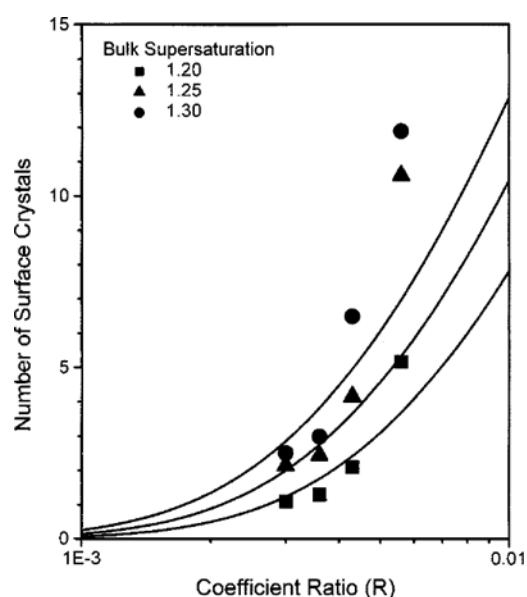

Fig. 4. Model prediction of number of surface crystals relative to variation in coefficient ratio between mass transfer and surface integration in crystal growth process. The proportional constants, a_1 and a_2 for the model equation [Eq. (7)] were fixed at 100.0 and 0.1, respectively. The experiment data were referred to Kim and Kim [1999].
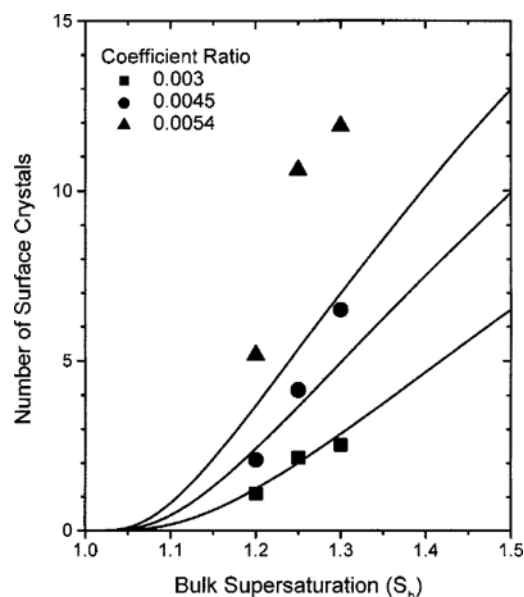

Fig. 5. Model prediction of number of surface crystals relative to variation in bulk supersaturation in recator. The proportional constants, a_1 and a_2 for the model equation [Eq. (7)] were fixed at 100.0 and 0.1, respectively. The experiment data were referred to Kim and Kim [1999].

at a fixed surface integration condition in the crystal growth, the solute concentration on the crystal surface will be highly built up, resulting in an increase of the interfacial supersaturation. Therefore, since the mass transfer rate is determined by the mass transfer rate coefficient depending on the hydrodynamic condition and the mass transfer driving force proportional to the concentration difference between at bulk and interface, the interfacial supersaturation is enhanced with an increase of the coefficient ratio (R) and bulk concentration (S_b). This prediction indicates that the secondary nucleation dependent on the interfacial supersaturation can also vary with crystallization conditions that have a direct influence on the coefficient ratio and bulk supersaturation, such as the reactant concentration and agitation speed. It should also be mentioned that the enhancement of the interfacial supersaturation could result from the inhibition of the surface integration.

The dependencies of the number of surface crystals on the coefficient ratio and bulk supersaturation were predicted, as shown in Figs. 4 and 5, respectively [Eq. (7)]. When comparing the model

prediction with experimental data, which were observed by Kim and Kim [1999, 2000], a direct match of the model variables of the coefficient ratio and bulk supersaturation with experimental variables of the agitation speed and reactant concentration was unfortunately impossible. This was because the kinetic parameters of the coefficients related with sodium fluoride crystal growth were basically unavailable in previous literature plus the bulk supersaturation of the reaction crystallization in a semi batch reactor was usually undefined in previous reports. However, based on trial and error, the bulk supersaturation and coefficient ratio corresponding to the crystallization condition set of the reactant concentration and agitation speed were estimated to fit the experimental data. In the estimation of the model variables it was assumed that only the mass transfer step in the crystal growth process was influenced by agitation, whereas the bulk supersaturation was predominantly determined by the reactant concentration. Thereafter, once the coefficient ratio at 700 rpm was estimated for the reactant concentrations, subsequent variations in the coefficient ratio relative to the agitation speed were calculated based on a correlation between the mass transfer coefficient and particle Reynolds number according to the power dissipation caused by the agitation [Fitchett and Tarbell, 1990]. The power dissipation in the reactor was calculated by using the power number for a Rushton reactor [MaCabe and Smith, 1976]. The estimation of the bulk supersaturation and coefficient ratio for each crystallization condition set is summarized in Table 1.

According to the proposed model, since surface crystal formation is promoted by the interfacial supersaturation, which is enhanced with an increase in the bulk supersaturation, and the coefficient ratio of the mass transfer to the surface integration, the number of surface crystals was predicted to increase. When the model prediction was compared with the experimental data [Kim and Kim, 2000], the predicted number of surface crystals deviated from the experimental data with an increase in the coefficient ratio. This result would appear to be due to the enhancement of the contact energy between
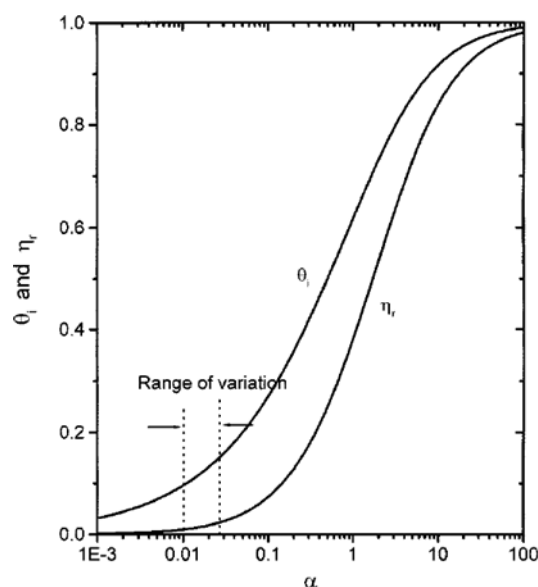

Fig. 6. Determination of rate-controlling step in crystal growth process of sodium fluoride.

crystals as well as the mass transfer with an increased agitation, as pointed out by Tai et al. [1975, 1992]. It should also be noted that the model equation [Eq. (7)] predicting the number of surface crystals on the mother crystal produced similar results to the equation estimating the number of secondary crystals generated by contact nucleation, as suggested by Tai et al. [1975]. Accordingly, even though the currently proposed model is described by using simplified equations based on surface nucleation and crystal growth mechanisms, the resulting predictions of surface crystal formation with variations in the crystallization conditions are consistent with the experimental data.

The effectiveness factor in the crystal growth process was related to the lump parameter, α, including two model variables of the coefficient ratio and the bulk supersaturation, as in Eqs. (9) and (12), respectively. As shown in Fig. 6, as α increased, the rate-determining step of the crystal growth shifted from the mass transfer to the surface integration. In addition, the interfacial supersaturation simultaneously approached the bulk supersaturation due to the fast mass transfer rate. In the present model, α, which was calculated from the estimated values of the coefficient ratio and bulk supersaturation for each crystallization condition set performed by Kim and Kim [2000], varied within a range of 0.01-0.027, thereby indicating the dominant control of the mass transfer step in the crystal growth of sodium fluoride. This may explain the reason why their experimental results of the number of surface crystals on the mother crystal were so sensitive to in the influence of agitation and the reactant concentration on the molecular transport.

CONCLUSION

Using two-dimensional secondary nucleation and two-step growth mechanisms, we developed a mathematical model to predict the number of surface crystals found on the mother crystal in the sodium fluoride crystallization. In this model, the number of surface crystals on the mother crystal is expressed as a function of the in-

Table 1. Summary of estimated values for model variables (R and S_b) with crystallization condition set [Kim and Kim, 2000] for model prediction of number of surface crystals*

Reactant conc. (mol/l)	RPM	ε (m²/s³)	R (k_c/k_r)	S_b (C/C_S)	α ($R/C_S(S_b-1)$)
1.75	700	0.48	3.0*10-3	1.2	0.015
	900	1.03	3.6*10-3	1.2	0.018
	1200	2.46	4.5*10-3	1.2	0.0225
	1500	4.80	5.4*10-3	1.2	0.027
2.5	700	0.48	3.0*10-3	1.25	0.015
	900	1.03	3.6*10-3	1.25	0.018
	1200	2.46	4.5*10-3	1.25	0.0225
	1500	4.80	5.4*10-3	1.25	0.027
3.75	700	0.48	3.0*10-3	1.3	0.015
	900	1.03	3.6*10-3	1.3	0.018
	1200	2.46	4.5*10-3	1.3	0.0225
	1500	4.80	5.4*10-3	1.3	0.027

*The proportional constants, a_1 and a_2 in model equation [Eq. (7)] were fixed at 100 and 0.1, respectively.

terfacial supersaturation, which is analogous to the secondary nucleation rate [Tai et al., 1975]. The interfacial supersaturation is predicted by the two-step growth mechanism. Therefore, as the bulk supersaturation and mass transfer coefficient in the crystal growth process increase, the interfacial supersaturation will be predicted to increase, thereby enhancing the surface crystal formation. When considering that the bulk supersaturation is generated by the reaction and the mass transfer coefficient is controlled by the hydrodynamic conditions surrounding the crystal, it was predicted that the number of surface crystals on the mother crystal would be facilitated by an increase in the reactant concentration and agitation speed. The model prediction of the surface crystal formation was found to be in good agreement with the experimental data.

ACKNOWLEDGEMENT

NOMENCLATURE

a_1, a_2 : proportional constants for surface crystal formation
C_b : bulk concentration
C_i : interfacial concentration
C_S : equilibrium concentration
D : diffusion coefficient
d : molecular diameter
$\Delta G'$: free energy change of two-dimensional embryo on mother crystal
J' : two-dimensional nucleation rate
k : Boltzmann constant
k_c : mass transfer coefficient
k_r : surface integration coefficient
L' : circumference of embryo
n : number of molecules contained in embryo
N_S : number of surface crystals on mother crystal
R : ratio of mass transfer coefficient to surface integration coefficient (k_c/k_r)
r : surface integration order
S_b : bulk supersaturation (C_b/C_S)
S_i : interfacial supersaturation (C_i/C_S)
T : temperature

Greek Letters

α : lump parameter for model of surface crystal formation $(R/C_S^{r-1}(S_b-1)^{r-1})$
θ_i : dimensionless interfacial supersaturation $((S_i-1)/(S_b-1))$
η_r : surface integration effectiveness factor

Superscript

* : critical state in secondary nucleation on mother crystal

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