MORPHOLOGY AND THE KINETICS
OF THE CRYSTAL GROWTH

M. Jakubczyk, G. Kopyciak

Institute of Chemistry and Environmental Protection, Jan Długosz University, al. Armii Krajowej 13/15, 42-201 Częstochowa, Poland

INTRODUCTION

Most of materials are soluble in a wide range of solvents and can be grown from solution by a variety of methods of temeratures close to ambient. The supersaturation for growth may be arhieved in a number of ways, including slow cooling of a saturated solution.

The mechanistic influences of the solvent are two stages: firsty by changing the total number of growth sites through modification of the surface energies and secondly by decreasing the fraction of sites available for growth as a results of solvent adsorption at the surface.The impurities present in mother phase lead to changes in growth rates and morphology of crystals. May be it adsorbet at kinks, ledges or terraces of a growning crystal face.

Adsorption of an impurity is belived to have effect on three parameters, namely, on the thermodynamic and kinetic terms involved in the growth models and on the crystal solubility. Some impurities are practically immobile after adsorption an the crystal face, while others are mobile and may easily desorb from the surface.

It is easy to realize two extreme cases of impurity particles are capable of adsorbing at binles while immobile impurity particles will mainly absorb at the surface terrace. However, in both cases some contributin due to adsorption at ledges is also possible.

The theoretical models if follows of growth prodiet opposite effects of impurities on growth kinetics.The overall morphology of a crystal consist of faces growing at the lowest rates. A change in the growth mechanism of face can occur with a change in the supersaturation used for growth. This may result in a change in the relative growth rates of different face appearing in the morphology, and onsequently the morphology of the growing crystal may undergo change with a change in the supersaturation used.

The process of the crystal growth kinetics was investigated using the Fokker-Planck equation. The use of the diffusion Fick equation to relate the surface concentration and diffusion requires the use of the modified surface diffusion coefficient which is $D = D_s(1+o(\beta))$ where: D_s – is a diffusion coefficient witch the absence of adsorption and desorption, $\beta = 1/\xi \tau_D$ is a ratio of relation time characterizing the diffusion surface ($1/\beta$) and desorption τ_D.

The basic kinetical process in the BCF theory is a (strong) surface diffusion. Adsorbing molecules from the solution to the surface diffuse along it to the terrace. They desorp along the tarrace to the kinks, where they build themselves into the lattice. The density of the absorbting molecules is an equilibrum value, so steps are not very good absorbents. They only keep the

number of the molecules necessary for the thermodynamic equilibrium. The exchange of the molecules by the adsorption and desorption is represented by the II Fick law.

$$D_s\, d^2n/dx^2 + c_\beta - n/\tau_D = 0 \qquad \text{for } x= \tfrac{1}{2}\,L \qquad (1)$$

where: n - is the density of the adsorbed molecules
c_β - is a constant proportional to the solution concentration

$$c_\beta = KN = KN^0(1+ \sigma) \qquad (2)$$

In the adsorption and desorption equilibrium state

$$c^0_\beta = KN^0 = n^0/\tau_D \qquad (3)$$

where: L - is the length of the terrace N - is solution concentration
n_0 - equilibrium surface concentration

For the low supersaturations σ, N is approximately equal equilibrium N^0. The equation (1) is an equilibrium flux, which contains the flux described by the I Fick law $j = - D_s\, dn/dx$. The Fick equation is limited to the macroskopic level. While, the Fokker - Planck one allows to describe the process of difuson on the microscopic level in more detail [1]. For the one-dimentional system the equation is the following

$$\upsilon\, \partial f/\partial x = \xi(\, kT/m\; \partial^2/\partial \upsilon^2 \; + 1 \; + \upsilon\partial/\partial\upsilon)f = \Omega f \qquad (4)$$

where: $f(x,\upsilon)$ is the density in the dimention position-rate and ξ is a cofficient related to the diffusion coefficient through the Einstein relationship $D_s = kT/\xi m$ where: m is molecule mass, Ω is an own function for the Hermite´a multinomial. The equation (4) solution, in a general, is

$$f = \sum a_s(x)\, H_s\,(\upsilon)\, \exp(-\upsilon^2/2kT)/(2\Pi kT)^{1/2} \qquad (5)$$

where: a_s – is a constant related with the temporary f, $H_s\,(\upsilon)$ are Hermite´a multinomials.

The equations (5) system of temporary values f for the simplified arrangements gives a solution of the adsorbed and desorpted flux quantites

$$j_+ = n^0(kT/2\Pi)^{1/2}\, [1 + \delta(2\beta\Pi)^{1/2}(1 + 1/2\beta)\, \mathrm{tagh}1/2L\alpha^{1/2}\, -\beta\sigma + o(\beta^{5/2}\,)] \qquad (6)$$

$$j- = n^0(kT/2\Pi)^{1/2}\, [\beta\sigma + (2\Pi\beta)^{1/2}\, \mathrm{tngh}1/2L\alpha^{1/2}- o(\beta^{5/2})] \qquad (7)$$

If a step is a perfect adsorbent then j- = 0. If σ and β are small j- is small as well. The flux difference $\Delta j = j_+ - j-$ describes the growth kinetics for the positive σ value

$$\Delta j = n^0 (kT/2\Pi)^{1/2} + n^0 \sqrt{k}T \ (3/2\sigma - 1) \ \beta^{1/2} \mathrm{tngh} 1/2 L\alpha^{1/2} \qquad (8)$$

The experimental werification of the solution was carried out using the kinetical data obtained from the in situ measurements.

EXPERIMENTAL

The applied model substance to investigate growth kinetics and morphology of crystal faces was the ammonium oxalate monohydrate. The direct observations of crystal growth were carried out due to a specially constructed set for a microscope and camera CCD connected with a computer [2]. To prepare the solution the demineralized water was used (2μS) as well as pure for the analysis $(NH_4)_2C_2O_4 \cdot xH_2O$ (produced by POCH). The solution with $\sigma = 0 \div 0.015$ flowed over the crystal surface (010).

The supersaturation of the solution was established using the curve of the ammonium oxalate solubility [3]. The temperature (in limits of $25°C$) was settled by
a computer program "Easy Temp" in a termostat "Julabo" with the exactness $0.05°C$. The shifting steps on the crystal surface were recorded by a PC computer.

RESULTS AND DISCUSSION

The characteristic elements of the micromorphology of the ammonium oxalate surface (010) changing during the growth are presented in Fig.1

Figure 1. The changing surface (010) of the ammonium oxalate crystal

From the recorded micromorphologies during changes it was possible to calculate the velocity of the steps movement (υ) and the slope of the hillock growth (p) (Fig.2) [2].
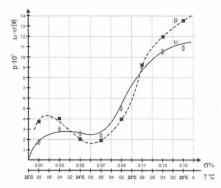
Figure 2. Dependences of the slope of the hillock growth (p) and the velocity of the step movement (u) on the supersaturation (σ).

Using these data we calculated the experimental flux Δj of the adsorbed particles versus the supersaturation (σ) Fig.3 presents the comparison of the experimental flux and the theoretical one calculated according to the equation (8).
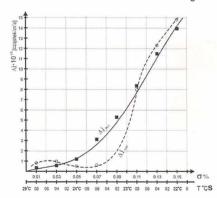

Figure 3. The comparison of Δj fluxes experimental and theoretical ones.

The obtained results prove that in the supersaturation range $\sigma = 0,03 \div$ 0,05 the velocity of the steps movement gets lower distinctly which disagreas with the theoretical establishments. The reference theoretical considerations concerning the influence of the impurities of the foreign ions show that they can slow down the steps movement [4]. In this case the impurities activate in this range of supersaturations.

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