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## MORPHOLOGY AND KINETIC OF CRYSTAL GROWTH

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Camera CCD has been applied to in situ study the (100) and (110) ammonium oxalate monohydrate (AO) growth kinetics in aqueous solution in the kinetic regime. From these data, the average step growth rate  $v$  has been determined as a function of relative supersaturation  $\sigma$ . The dependence  $v(\sigma)$  is found to be linear, demonstrating the unimportance of surface and bulk diffusion. The supersaturation dependence of activities for various complex dislocation sources have been directly demonstrated.

*Key words:* crystal growth, ammonium oxalate.

The crystal growth may occur only in the metastable region, whose width is limited from one by the curve of solubility and from the other side by such a value of supersaturation where three-dimensional nucleuses are intensely created and outside this region the monocrystals cannot be obtained. Growth of a perfectly smooth face may occur due to the build in of a growth unit into the kinks existing on the surface owing to two-dimensional nucleation. When a monomolecular layer covers the face, renucleation appears, which is a source of reproducing steps. The growth process should repeat in a discrete way. Creation of the two-dimensional stable nucleus on the perfect face requires overcoming the activation energy [1].

All models of the two-dimensional nucleation need the observation of the growth in the supersaturations  $\sigma > 2,0\%$ . However, the crystal growth occurs in lower supersaturations because, of the dislocations. The dislocations having Burger's component perpendicular to the growing face are the permanent source of the kinks necessary for the growth. The growth process follows of the unfinished process of joining, the growth hillock unit around the dislocation to the uncovered step. Hence, a growth hillock in a spiral shape creates [2, 3]. The hillock is made of series of steps, which far away from the centre can be treated as a series of straight parallel steps. In this paper the dependence between the number of dislocation and the rate of the face growth of ammonium oxalate monohydrate (AO) was proved.

The experimental procedure for the growth of ammonium oxalate monohydrate has been reported in our previous paper [4]. It consists of a flow system in which the crystals are grown under a negligible influence of the bulk diffusion resistance. The growing crystals were fixed on the stand in the thermostatic vessel made in plexi in the visual of the microscope lens. On the microscope a CCD camera was fixed with a computer. Small self-nucleated crystals with dimensions between 4 and 5 mm along the [001]

direction growth at temperature of about 25°C from solutions by solvent evaporation were used as seeds. The solutions were prepared from double distilled water and analitically pure AO with 0,005 % SO<sub>4</sub>, 0,001 % Cl, 0,001 % Pb and 0,00055 % Fe impurities.

Supersaturation was created by a temperature decrease and was calculated to by  $\sigma = C - C_0 / C_0$ , where the actual and equilibrium concentration,  $C_0$  and  $C$  respectively, were given in mass fractions.. The supersaturations used for the growth were between 1 and 5 %.

The equilibrium concentration  $C_0$  was determined on the basis of the data from the paper [5]. The growth solution was being pumped parallelly to the growing face. The linear velocity of the solution as related to the face was ~ 1 cm/s (in the laminar range flow). The temperature growth conditions were provided by a termostate MV-4 computationally programmed (program Easy Temp) with the approximacy 0,02 °C.

The growth of faces (110) and (100) was observed (Fig. 1). Changes of the growing surface (the slope of the growth hillock) were recorded using a camera CCD on the computer.

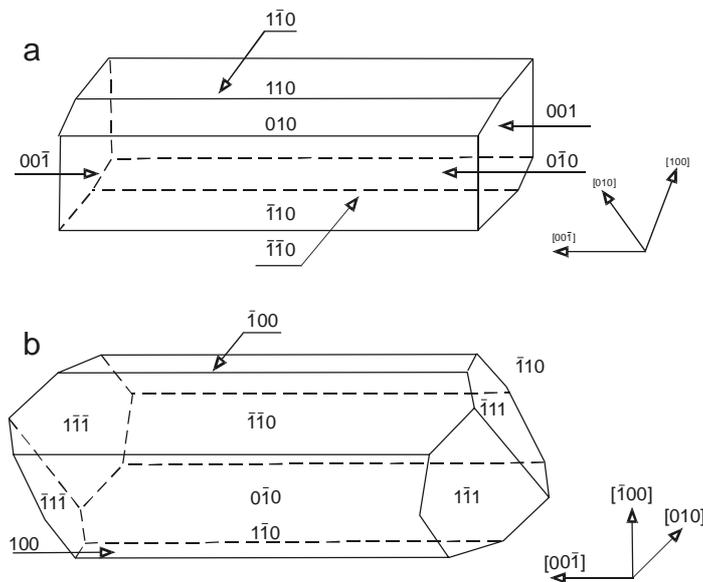


Fig. 1. Schematic diagram of habits of AO crystals at *a* low and *b* high supersaturations

Fig. 2, 3 shows the changes in the relief of the (110) *a* and (100) *b* face with an increase in  $\sigma$ . For low  $\sigma$ , the dislocation hillock is of the regular shape characteristic of the kinetic grow mode. The velocity of steps forming the hillock increases near the edges, the steps are bending and moving towards one another at the front edge. The inny effect consists in the following. The surface near the back edge loses its stability and macrosteps are formed. Bending of the step front due to the presence of a gradient in  $\sigma$ , and correspondingly of the step velocity along the surface, is quite a common phenomenon. Its specific features strongly depend on the number and mutual

arrangement of the dislocation hillocks and their distribution over the surface. Bending of elementary steps and the macrostep formation are most clearly pronounced in range where function  $v(\sigma)$  nonlinear and it has high values of  $\partial v/\partial \sigma$  derivatives.

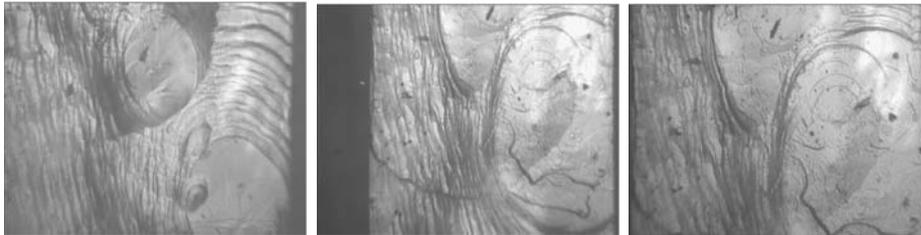


Fig. 2. The steps movement on the slope of the hillock on the face (110) AO every 20 min with  $\sigma = 4\%$  and temperature  $25^\circ \text{C}$ .



Fig. 3. The steps movement on the slope of the hillock on the face (100) AO every 20 min with  $\sigma = 4\%$  and temperature  $25^\circ \text{C}$ .

According to the classic theory  $v(\sigma)$  is a linear dependence. However, there are exceptions from the linear dependence  $v(\sigma)$ . The supersaturation gradient along the surface provides the formation of the gradient in velocity  $v$ . Therefore it is natural to consider the character of the function  $v(\sigma)$ . The corresponding curves obtained in the kinetic growth mode of the face are shown in Fig. 4.

These functions are essentially nonlinear for low  $\sigma$  ( $\sigma < \sigma^*$ ), the slope of the curves  $v(\sigma)$  is small, then it drastically increases, reaches the maximum and for  $\sigma \gg \sigma^*$  becomes constant. In other hand, the function  $v(\sigma)$  becomes a straight line passing through the origin. As was to be expected, the above data indicate that the most pronounced manifestation of hydrodynamical effects in the surface morphology is observed in the supersaturation range corresponding to the maximal values of  $\partial v/\partial \sigma$ . Considering the loss of the morphological surface stability as a process caused and supported by local fluctuations in the surface supersaturation and the concentration of absorbed impurities. It is also clear that at the steep surface slopes where the step spacing is smaller, the coagulation occurs with higher probability. If there is a surface gradient in  $\sigma$ , then the steps moving towards lower  $\sigma$  are more inclined to coagulation than the steps propagating towards higher  $\sigma$ . If the gradient in  $\sigma$  is given by the solution flow and decreases with the distance from the front edge, macrosteps are more readily formed in the step echelon moving along the flow.

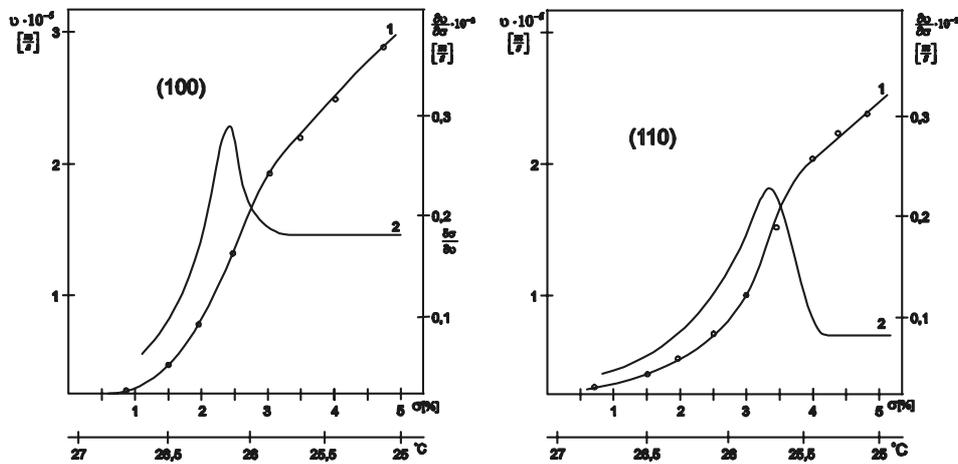


Fig. 4. The effect of supersaturation on  $v$  (curve 1) and on  $\partial v / \partial \sigma$  (curve 2) for steps parallel to (100) and (110) on the AO surface

These experimental dependences are caused by the geometry of the impurity present on the step surface and its action on the step movement. For different possible geometric situations the step movement  $v(\sigma)$  takes a determined value because the impurity itself can be a source of the step and it can diminish the size of the critical nucleus. As it was proved theoretically [6] the slope of the surface of the growth  $p(\sigma)$  can change both with and without the impurity. The result of the present study consists in the experimental establishment of the fact that the loss of the morphological stability of the growing crystal surface and the related loss of the crystal perfection are determined not only by the spatial variation of the surface supersaturation but also by other factors, the most important of which is the character of the  $v(\sigma)$  dependence. In case of the screw dislocations, the growth hillocks depending on the thermodynamic conditions, are generally characterised by a changeable slope with either a positive or negative curvature. As it can be seen from the presented data, the cause of these changes are the impurities present in the growth solution.

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## МОРФОЛОГІЯ І КІНЕТИКА РОСТУ КРИСТАЛІВ

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Досліджено кінетику росту водного розчину моногідрату оксалату амонію в напрямках (100) та (110) у кінетичному режимі. Отримані дані дали змогу оцінити середню величину кроку підвищення  $v$  як функцію відносного перенасичення  $\sigma$ . З'ясовано, що залежність  $v(\sigma)$  є лінійною, що свідчить про незначний вплив поверхні та об'ємної дифузії. Показано залежність від перенасичення активності різних джерел дислокацій.

*Ключові слова:* ріст кристалів, оксалат амонію.

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