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THE INVESTIGATION OF KINETIC GROWTH {100} FACES OF ADP CRYSTALS IN THE RANGE OF LOW SUPERSATURATIONS

R.Ristić, B.Žižić, R.Milinković

Institute of Physics, PMF and Laboratory of Electron Microscopy (Belgrade)

INTRODUCTION

In the determination of growth rate /R/ of ADP microcrystal faces {100} in the direction [010] great scattering of the experimental points on the graph $R=f/\sigma/$ which can not be accounted for by measurement errors has been found. Alexandru [1] has found a similar effect during the investigation of ADP crystal growth and solution kinetics in the range of low supersaturation as well as Booth and Bucley [2] during the investigation of ethylene diamine tetramine /EDT/ crystal kinetics. At the same supersaturation and temperature growth rates differed by a factor of 2 to 3.

Great scattering of the experimental results on the graph $R=f(\sigma)$ should be considered as a consequence of different values for the activities of dominating dislocation groups on the particular microcrystal faces. Different values of the activite cause different faces of the same crystal or even the faces of different crystals with same indexes under the same experimental conditions to have different dependences $R=f(\sigma)$.

The aim of this paper is to assess the extreme values of the activities of dominating dislocation groups on the faces {100} of a number of ADP microcrystals depending on the supersaturation in the range of $0.01 \leq \sigma \leq 0.06$ under particular experimental points scattering on the graph $R=f(\sigma)$ causes various activities of the dislocation groups on the crystal faces.

EXPERIMENT

ADP microcrystals grew on the bottom of a crystallization cell in which the constant temperature ($23{,}00 \pm 0.02^{o}C$) as well as the constant solution supersaturation was maintained. The flow of the solution was 3 ml/min.

The measurements of the crystal face displacement were performed under an optical microscope with transparent light under a total magnification of 150 x. A change of distance of the crystal faces {100} in the direction [010] was measured for 3-5 hours under the carefully controleed conditions of supersaturation σ= const, temperâture T=const., solution flow q=const., The measurements were performed on 15 different microcrystals chosen in the following way: Out of several microcrystals formed during the cell cover lifting were chosen those of which the directions [001] coincide with the solution flow direction what provides the same conditions for the mass transfer on faces {100}. The growth of three chosen microcrystals was measured in the course of one measurement.

The influence of the change of the solution flow through the cell on the microcrystal growth rate was not noted.

RESULTS AND DISCUSSION

The dependance $R=f(\sigma)$ in the supersaturation range $0,01 \leq \sigma \leq 0,06$ is presented in Fig.1. The rates are calculated by applying the method of "the least squares" and the use of computer. The measurement results indicate that the crystals grow in the three. Well-differentiated and the most possible activities.

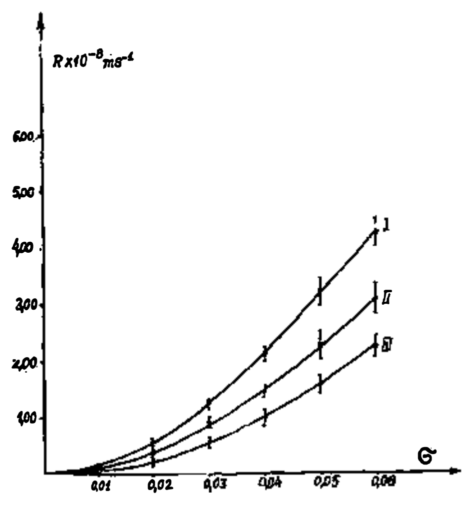

Fig. 1

According to the BCF [3] theory, the ratio of the growth rate R and the supersaturation is given by the equation:

$$R= C\frac{\sigma^2}{\sigma_1} tgh\frac{\sigma_1}{\sigma} \qquad (1)$$

where C and σ_1 are the characteristic parameters. C defines the slope of the linear part of the curve $R=f(\sigma)$ and σ_1 depends on the following physical values:

$$\sigma_1 = \frac{9,5}{\varepsilon}\frac{\gamma}{kT}\frac{a}{x_s} \qquad (2)$$

where ε is the activity of a dominant dislocational group determining the growth rate. If the dislocations in the group are of the same sign and each at a distance shorter than $2\pi\rho_c$, where ρ_c is the critical radius of a nuclei, their activity will shall be greater than of the isolated dislocation:

$$\varepsilon = \frac{n}{1+\frac{L}{2\pi\rho_c}} \tag{3}$$

where n is the number of dislocations in the group and L the distance between the extreme dislocations, k the Boltzmann constant, T the temperature, a the shortest distance between the neighbouring growth units (molecules), x_s the mean movement of growth units on the crystal surface and γ the edge free energy of a growth unit in a step.

The characteristic parameters C and were first determined by means of the graphical method [4]. By approximation of a part of the curve I, fig.1, by a line that does not pass through the coordinate origin:

$$R \approx R_2 = Ca\sigma + Cb \tag{4}$$

in the supersaturation range $0,035 \leq \sigma \leq 0,06$ the intercept formed by that line on the abscis $\sigma_0 = (2,10 \pm 0,05) \cdot 10^{-2}$ as well as its direction coefficient $C_2 = \ =1,1 \cdot 10^{-6} ms^{-1}$ were determined. In the mentioned supersaturation range according to the ratio $\frac{\sigma_0}{\sigma_1} = 0,270$, while the parameters of the line (4) are: a=1,026, b=-0,28 with the approximation error of 1,069% that is less than the experimental error of this work. On the ba basis of the data mentioned characteristic parameters were determined.

$$\sigma_1 = \frac{\sigma_0}{0,270} = 7,78 \cdot 10^{-2} \quad and \quad C = \frac{C_2}{a} = 1,07 \cdot 10^{-6} ms^{-1}$$

The value of the C parameter so determined was used as the starting value for determination of the values of curves σ_{1i}^{I}, σ_{1i}^{II} and σ_{1i}^{III} fig.1, by use of a computer and the equation:

$$\sigma_{1i} = C\frac{\sigma_i^2}{R_i} tgh \frac{\sigma_{1i}}{\sigma_i} \tag{5}$$

where σ_i is the value of the particular supersaturation and Ri the growth rate at that supersaturation. Since the calculated values σ_{1i}^{I} σ_{1i}^{II} and σ_{1i}^{III} are almost equal it can be assumed that their average value ($\overline{\sigma_1^{I}}$, $\overline{\sigma_1^{II}}$ and $\overline{\sigma_1^{III}}$) characterizes growth of the faces {100} of the corresponding microcrystals.

These parameters were used in the calculation of the characteristic parameter C for all three curves according to the equation (1) Values of the so calculated characteristic parameters C and the corresponding average values of the parameters $\overline{\sigma_1}$ are shown in Table 1.

As can be seen from Table 1, characteristic parameter C has an almost equal value for all three curves i.e. for microcrystals with different values of the activity the deviations are ± 3.1 %. The values for are different for curves I, II and III what according to the equation (2) corresponds to the different activities ε. If we assume that the parameters μ, T, a and x_s are same for all microcrystals measured then according to equation (2) it is possible, to assess the activity of the dominating dislocation groups of microcrystal by comparison of the values calculated for $\overline{\sigma}_1^{I}$, $\overline{\sigma}_1^{II}$ and $\overline{\sigma}_1^{III}$.

TABLE 1

SEE: Fig. 5	C [m s⁻¹]	$\overline{\sigma}_1$
CURVE I	$0.99 \cdot 10^{-6}$	$6.7 \cdot 10^{-2}$
CURVE II	$0.95 \cdot 10^{-6}$	$9.8 \cdot 10^{-2}$
CURVE III	$0.94 \cdot 10^{-6}$	$14.0 \cdot 10^{-2}$

According to [5] the most probable activity in case where $L \ll 2\pi\rho_c$ see eq. (3) is equal to the number of dislocations in a group and equals 5. In our investigations only a few microcrystals had the activity ε greater than that of the microcrystals comprised by curves I [no microcrystal of the activity between those of microcrystals comporised by curves I, II and III was found]. At the supersaturation σ=0,01 the face growth rates were very small and could not be well differentiated among groups. From the results of our measurements it is evident that the microcrystals grow with the definite discontinual values of t the activity what gives ground for the assumption that the activity on the faces {100} of microcrystals comprised by curves I, II and III is 5, 4 and 3 or 4, 3 and 2 or 3, 2 and 1 respectively. Assuming that μ, T, a and x_s are of the same value for all one can determine the activity of the microcrystal.

The quotients of parameters $\overline{\sigma}_1$ and of the dominant dislocation groups assumed activities that would correspond to the values of $\overline{\sigma}_1$ are shown in Table 2. With respect to the results shown in Table 2 the most suitable values of the activities on microcrystal faces {100} are 4, 3 and 2 respectively. Small deviations of the parameter C for all three activities of microcrystals growth and a good agreement of the experimental curves I,II and III with equation (1) do not completely confirm that the ADP microcrystal growth deve-

TABLE 2

Quotients of parameters $\overline{\sigma}_1$	Quotients of the assumed activities	Quotients of the assumed activities	Quotients of the assumed activities
$\frac{\overline{\sigma}_1^{II}}{\overline{\sigma}_1^{I}}=1.42$	$\frac{3}{2}=1.50$	$\frac{4}{3}=1.33$	$\frac{2}{1}=2.00$
$\frac{\overline{\sigma}_1^{III}}{\overline{\sigma}_1^{I}}=2.08$	$\frac{4}{2}=2.00$	$\frac{5}{3}=1.66$	$\frac{3}{1}=3.00$
$\frac{\overline{\sigma}_1^{III}}{\overline{\sigma}_1^{II}}=1.46$	$\frac{4}{3}=1.33$	$\frac{5}{4}=1.25$	$\frac{3}{2}=1.50$

lops by the BCF surface diffusion [3]. From the experimental value of C, the slope of the linear portion of the R(σ) curve, and according to [5] the value of the activation free energy of the dehytratization ΔGdeh=12,9 $\frac{kcal}{mol}$ is calculated. This value agrees with the one determined by Davey [6], ΔG deh=12,6$\pm$0,5 $\frac{kcal}{mol}$ for the growth of ADP crystal faces {101}. On the basis of values determined for parameters C, σ_1 and ΔGdeh. it can be concluded with certainty that the process of ADP microcrystal face {100} growth develops by the surface diffusion model of the spiral growth.

CONCLUSION

The method for measurement of the growth rate of individual microcrystal faces at constant values of temperature and supersaturation is developed. Measurements were performed on the microcrystals of 0,03-0,2 mm which had a high rate of mass transfer toward microcrystal face with respect to the rate of face growth due to what was kept constant. On the basis of the properties of the functions $R=f(\sigma)$ the parameters $C, \bar{\sigma}_1^{I}, \bar{\sigma}_1^{r}, \bar{\sigma}_1^{B}$ and ΔGdeh were calculated.

The scattering of experimental points $R=f(\sigma)$ is explained by discrete values of the dominant dislocation groups of which the most probable value is 4, 3 and 2. It is determined that the process of ADP crystal face {100} growth develops by the surface diffusion model of the spiral growth.

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