THE KINETICS OF GROWTH AND THE MORPHOLOGICAL INSTABILITY OF ZINC SINGLE CRYSTALS*

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The effect exerted by diffusion upon the kinetics and morphological stability of zinc single crystals during growth from vapour phase in the presence of argon is studied. The shift of the basal face in normal direction and the growth of the edge of the same face as a function of time is checked at constant temperature and constant supersaturation at high vacuum or argon pressure 666-33330 Pa. Linear and parabolic dependences of the crystal size R as a function of the time t, respectively of the length of the basal edge a as a function of the time as well as the kinetic critical size R_k, respectively a_k are established. In agreement with the isotropic theory of Chernov and Cahn, zinc single crystals with sizes R smaller than R_k grow in a kinetic regime, while those with sizes R larger than R_k grow in a diffusion regime. It is shown that the results of the kinetic investigations are in good agreement with data obtained by morphological studies.

Introduction

The rate of crystal growth generally depends on the transport of matter within the bulk of the parent phase and the elementary processes upon the surface of the crystals. The consideration of the surface processes only during growth in vacuum and the retention of the polyhedral form has been shown by Kaischew, Stranski et al [1, 2]. The predominant effect of bulk diffusion has been studied by Chernov [3] and Cahn [4]. Nanev and Iwanov [5, 6] have established that during the growth of zinc single crystals from a vapour phase in the presence of hydrogen and argon, when a certain size is surpassed, a depression appears upon the smooth basal face. The transition from polyhedral to skeleton growth hitherto has been mainly investigated by a morphological approach. The present paper is aimed at the confirmation that diffusion in a vapour phase affects not only the morphological stability, but also the kinetics of crystal growth.

Experimental

The kinetic and morphological investigations were carried out with zinc single crystals prepared by the method of Stranski and Kaischew, described earlier [2, 5].

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By this method the single crystals are obtained in a glass ampoule from a molten droplet using a furnace with a cooling finger. A constant temperature difference ΔT between the furnace and the finger determined the supersaturation σ. The zinc single crystals were grown in a vapour phase at a constant temperature of the furnace $T = 400°C$, $\Delta T = 20°C$ ($\sigma = 0.6$) in the presence of highly purified argon at the following pressure : 666, 1333, 6666, 13332, 19998 and 33330 Pa.
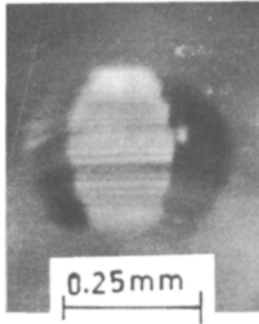

Fig. 1. Zinc single crystal grown in the presence of argon, $P_{Ar} = 1333$ Pa
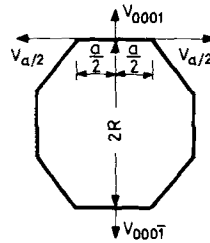

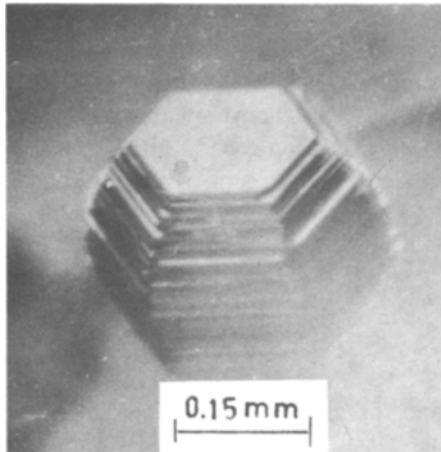Fig. 2. Schematic representation of zinc single crystal

Fig. 3. Zinc single crystal with a smooth basal face

The kinetic studies included the measurement of the shift of the basal face in normal direction as a function of the time t [7]. The measurements were carried out as the single crystals lay with one of their prismatic faces upon the glass ampoule and the two {0001} faces were positioned laterally (Fig.1). Thus the distance between the two opposite basal edges $2R$ was measured (Fig.2).

At each pressure of argon used in the experiments, as well as at vacuum $1.33 \cdot 10^{-4}$ Pa, we carried out 10–15 separate measurements using crystals with sizes within the range $R = 0.4 \cdot 10^{-2}$ to $3.5 \cdot 10^{-2}$ cm. Under the same experimental conditions we carried out 10 to 20 separate measurements of the growth of the edge of the basal face a as a function of time t [8]. In the latter case the {0001} face was situated on the upper side of the single crystals (Fig.3). The size a had the same values as that of R. Simultaneous measurements were made of the change of R and a with time t using identical crystals (Fig.2).The morphological observations of the {0001} face were also carried out simultaneously with the measurements of the increase of the edge length a as a function of the time t [8].

Results and discussion

It has been established that the size R of small zinc single crystals increases linearly with the time t (Fig.4).
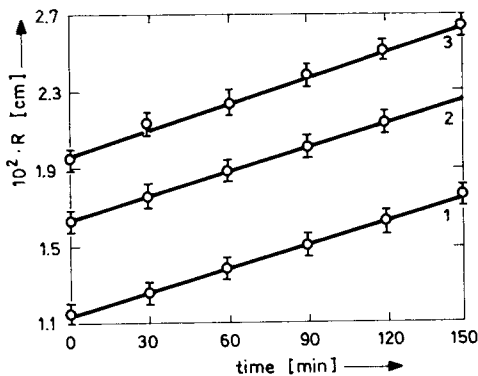

Fig. 4. The size R as a function of the time t of three zinc single crystals 1, 2, 3, grown at $P_{Ar} = 1333$ Pa. The error bar shows the accuracy of the measurements

The linear relationships show that the growth rate is constant. A crystal dimension region exists, where the linear $R(t)$ relationship is transformed into a non-linear one. The non-linear $R(t)$ curves were approximated to $R^2 = a_1 + b_1 t$ -type parabolas, where a_1 and b_1 are constants. Fig.5 shows the relationship between R^2 and t at $P_{Ar} = 6666$ Pa.
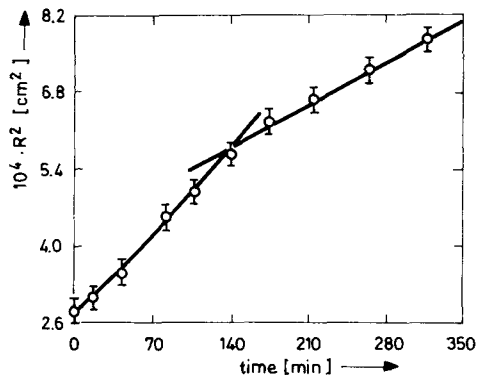
Fig. 5. R^2 as a function of the time t of a zinc single crystal, grown at $P_{Ar} = 6666$ Pa. The intersection point of the curves determines the critical size R_k

It can be noted that the last 5 points are well fixed on a straight line, confirming that the $R(t)$ relationship in this region is parabolic. All graphical relationships comprising two regions displayed an abrupt transition. From the intersection point of the two separate curves of a given graph the kinetic critical size R_k was determined [7] (Fig.5). When the initial size of zinc single crystal R_0 was larger than the critical size R_k, only parabolic $R(t)$ dependences were obtained. It follows from the parabolic relationship that the growth rate is not constant and depends on the size R. Under high vacuum conditions only linear $R(t)$ dependences were obtained, i.e. the single crystal growth proceeded at a constant rate.

Similar relationships were obtained when the size a was plotted with the time t : linear and parabolic $a(t)$ [8].

The simultaneous investigation of the $R^2(t)$ and $a^2(t)$ relationships established that both curves at the same moment change their initial shape into a linear one. This result shows that the kinetic critical sizes R_k and a_k [8] fix an identical transition moment in the growth of the $\{0001\}$ face of the zinc single crystals.

The results from the kinetic investigations were considered by applying the isotropic theory of Chernov [3] and Cahn [4]. According to the theory, the growth of a spherical crystal from an unstirred solution under diffusion transport conditions proceeds in two stages, depending on the value of the radius R : kinetic and diffusion. The kinetic regime is characterized by a constant rate of growth and a linear increase of the size R with time t. During a diffusion regime the growth rate is not constant and depends on the crystal size R. Under this growth regime the radius of the sphere R changes with time t according to a parabolic relation.

In agreement with the isotropic theory [3,4], we accept that the size R of the zinc single crystals is the radius of the sphere, inscribed between the two basal faces (Fig. 2).

The results from the kinetic investigations were compared with the basic conclusions of the isotropic theory. The observed linear $R(t)$ and $a(t)$ relationships and the constant growth rate suggest that the small size zinc single crystals grow in a kinetic regime. The establishment of parabolic $R(t)$ and $a(t)$ relationships and rates dependent on the size R show that larger single crystals grow in a diffusion regime. Consequently, the transition between the two growth modes begins at the kinetic critical size R_k and a_k, respectively.
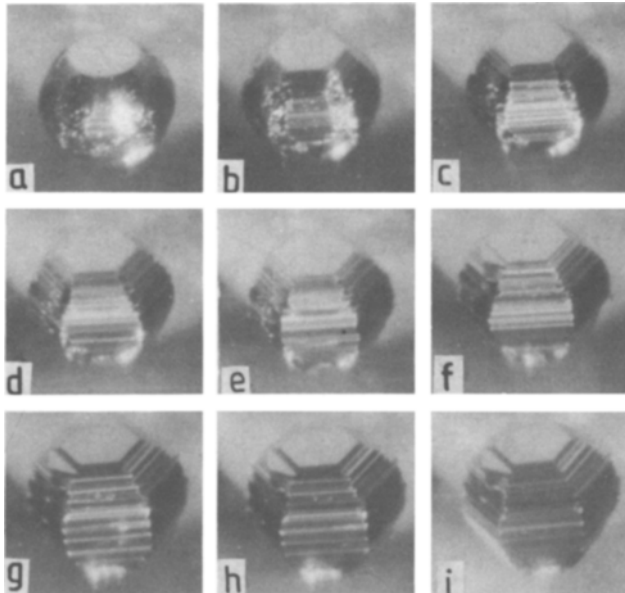

Fig. 6. Consecutive growth stages of a zinc single crystal at $P_{Ar} = 13332$ Pa, magnification 25 X

Table I

Values of V, β, D, R_k and R_{th}

P_{Ar} [10^3 Pa]	V [10^{-7} cm/s]	β [cm/s]	D [cm^2/s]	R_k [10^{-2} cm]	R_{th} [10^{-2} cm]
0.666	16 ± 3.5	191.38	4.72 ± 1.0	3.00 ± 0.35	2.46
1.333	10 ± 2.0	119.61	1.79 ± 0.5	2.60 ± 0.30	1.49
6.666	6 ± 1.5	71.77	0.77 ± 0.3	1.90 ± 0.35	1.07
13.332	2.9 ± 0.4	34.68	0.41 ± 0.2	1.65 ± 0.35	1.18
19.998	2.6 ± 0.9	31.10	0.248 ± 0.05	1.50 ± 0.20	0.79
33.330	1.6 ± 0.4	19.13	0.088 ± 0.05	< 0.78	0.46

The values of the growth rate V and the kinetic coefficient β were calculated by using the basic relationships of the isotropic theory and the slopes of the $R(t)$ curves, while the parabolic $R(t)$ graphs served for the evaluation of the diffusion coefficient D [7]. The V and β values characterize the growth mode during predominant surface processes, while D values are relevant when diffusion is the rate determining factor. Data of V, β and D are presented in Table I. The calculated data of V and D are not in agreement with literature data given by Parker et al [9] for V in vacuum and Redko and Kosinar [10] in the case of D.

The theoretical critical size R_{th} when the transition from kinetic to diffusion regime begins was calculated from the ratio between the values of D and β. The comparison of the values of the critical sizes R_k and R_{th} (Table I) shows that the agreement between theoretical and experimental data is fairly good. The R_k data represent the first experimental proof of the isotropic theory [3,4].
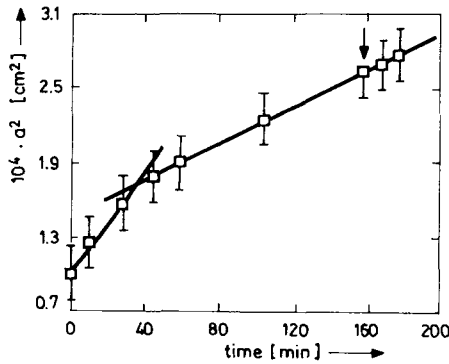

Fig. 7. a^2 as a function of the time t of a zinc single crystal shown in Fig. 6

We presume that during the transition from a kinetic to a diffusion regime of growth, surface changes occur upon the basal face. This presumption was checked by carrying out simultaneous kinetic and morphological studies using the same crystal. The zinc single crystals were oriented so as to fix the {0001} face on the top, as shown in Fig. 3. A similar orientation offered a possibility to measure the growth of the edge of the basal face a with time t, simultaneously observing the changes upon the surface of the face. At the moment when a depression appeared upon the basal face, we determined the observed morphological size a_m. Fig. 6 provides an illustration of consecutive growth of a zinc single crystal. The comparison between the plotted $a^2(t)$ dependence (Fig. 7) and Fig. 6 shows that the size a_k corresponds to Figs. 6c, 6d while a visible depression is not formed until Fig. 6g. The vertical arrow shows the moment when the size a_m is attained. It can be noted that the sizes a_k and a_m do not coincide. In fact this discrepancy is fictitious, since at the moment

of transition from a kinetic to a diffusion regime, the morphological stability of the face is disturbed. However, at the magnifications we used in the investigations, the microscopic changes upon the basal face were invisible. Only after the crystal was grown and the surface changes became macroscopic we were able to check the morphological size a_m.

Conclusion

The investigation of zinc single crystal growth in the presence of argon shows that as a result of the effect of diffusion in the vapour phase, when a certain size of the crystals is reached, a transition from kinetic to diffusion regime begins and the morphological stability is lost.

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