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L. A. BOROVINSKII, A. N. TSINDERGOZEN

1968

SovietRxiv

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UDC 548.5

CRYSTALLOGRAPHY

L. A. BOROVINSKII, A. N. TSINDERGOZEN

ON THE THEORY OF THE GROWTH OF CRYSTAL FACES BY THE POLYNUCLEAR MECHANISM

(Presented by Academician A. V. Shubnikov, 24 IV 1968)

In the theory of crystal growth by the mechanism of formation of two-dimensional nuclei, it is often assumed that each new layer of a crystal face is formed as the result of the spreading of a single two-dimensional nucleus. This corresponds to the assumption that the time required for a nucleus to spread over the entire area of the face is much less than the mean time between the appearance of two nuclei. Such an assumption is by no means always fulfilled. A theory of growth in which this assumption is abandoned is considered in greatest detail in Nielsen' s book ([1]). He considers the polynuclear growth of a face on the basis of mathematical modeling of the growth process.

In the present work we propose an analytical formulation of the problem and its solution by numerical integration of the resulting equation. The normal displacement of the crystallization front of a face with the formation of any number of two-dimensional centers in each layer is considered as a single probabilistic process, in which the growth of each subsequent layer is determined by the growth of the preceding ones.

Let us formulate the assumptions adopted in our statement of the problem. We shall neglect the boundedness of the face, regarding its linear dimensions as infinitely large. The physical conditions at all points of the growth front are assumed to be constant at any moment of time. We shall regard the probability of formation of a specified number of two-dimensional nuclei on a given plane portion of a layer during a given interval of time as depending only on the area of the portion and on the magnitude of the time interval. We assume that a two-dimensional cluster larger than the critical size, whose probability of dissolution may already be neglected, is still so small that it may be regarded as point-like. For an infinitely small portion of a layer ds and time interval dt, the probability of formation of such a cluster will be taken equal to

$$dW = \alpha\, ds\, dt, \tag{1}$$

where α is a coefficient depending on the growth conditions and, consequently, constant when these conditions are unchanged. We assume that the two-dimensional clusters have the form of a circle and spread continuously in all radial directions with constant velocity c. Since several layers may spread simultaneously, the crystallization front will be stepped. The layers are numbered by the index n, taking the values $0, 1, 2, ...$ The zeroth layer is assumed to be completely filled at the initial moment of growth, i.e., at the time $t_0 = 0$ the face is regarded as absolutely smooth. As the principal function characterizing the displacement of the crystallization front of a face, we shall consider the probability that the front of an arbitrary n-th layer has reached, by the time t, an arbitrarily chosen point of the layer (for layers of infinite dimensions such a function, obviously, does not depend on the choice of the point of the layer). We denote this probability by $f_n(t)$. We shall derive an equation relating $f_n(t)$ and $f_{n+1}(t)$.

If it is known that by the time τ the crystallization front of the $(n + 1)$-st layer has not yet passed through the point (x, y), then the probability of the occurrence

of a nucleus of the $(n + 1)$-st layer in some neighborhood of this point of area Δs during the time interval $(\tau, \tau + \Delta\tau)$ is, obviously, equal to the product of expression (1) by the probability that by the time τ the n-th layer has already become sharpened at the point (x, y):

$$\Delta W_{n+1} = 1 - \alpha f_n(\tau)\Delta s\, \Delta\tau. \tag{2}$$

Accordingly, the probability that no nucleus of the $(n+1)$-st layer arises on the same area during the same time interval is equal to

$$\Delta W'_{n+1} = 1 - \alpha f_n(\tau)\Delta s\, \Delta\tau. \tag{3}$$

For definiteness, we shall consider the point $(0, 0)$ of the $(n + 1)$-st layer. Obviously, the front of normal crystallization will pass through this point by the time t if in the $(n + 1)$-st layer there arises at least one nucleus whose time of appearance τ and point of appearance (x, y) belong, in the space x, y, τ, to the cone Q defined by the inequality

$$\sqrt{x^2 + y^2} < c(t - \tau). \tag{4}$$

Taking (3) into account, the probability that the point $(0, 0)$ is not captured by the $(n + 1)$-st layer by the time t is expressed as

$$\Delta W'_{n+1} \cong \prod_i [1 - \alpha f_n(\tau_i)\Delta\gamma_i], \tag{5}$$

where $\Delta\gamma_i$ is an element of the volume of the above-mentioned cone. Passing to the limit as $\max \Delta\gamma_i \to 0$, after simple transformations we find

$$W'_{n+1} = \exp\left[-\alpha \iiint_Q f_n(\tau)\, d\gamma\right]. \tag{6}$$

Carrying out the integration with respect to the variables x, y and passing to a dimensionless unit of time equal to $\alpha^{-1/3}c^{-2/3}$, i.e., putting $\tau' = \tau\alpha^{-1/3}c^{-2/3}$, we obtain:

$$W'_{n+1} = \exp\left[-\pi \int_0^{t'} (t'-\tau')^2 f_n(\tau')\, d\tau'\right], \tag{7}$$

where t' is the time measured in the new dimensionless units. In meaning, $f_{n+1} + W'_{n+1} = 1$. Hence we obtain the equation

$$f_{n+1}(t') = 1 - \exp\left[-\pi \int_0^{t'} (t'-\tau')^2 f_n(\tau')\, d\tau'\right]. \tag{8}$$

Let us note some properties of the functions $f_n(t')$. Obviously, $f_0 \equiv 1$. For $n > 1$, each of the functions $f_n(t')$ is a monotonically increasing function of time from zero. As $t' \to \infty$, $f_n(t') \to 1$. For the established process the equality

$$f_{n+1}(t') = f_n(t' - T). \tag{9}$$

must hold. The quantity T is to be determined. It represents the mean time of formation of one new layer in the process of stationary growth. The integral-recurrence equation (8) gives, in principle, the possibility of finding the function $f_n(t')$. By analytical integration one easily finds only

$$f_1(t') = 1 - \exp\left(-\frac{\pi}{3}t'^3\right). \tag{10}$$

Each of the functions $f_n(t')$ gives the degree of filling of the n-th layer at the time t'. The analytically found $f_1(t')$ is the solution, in the two-dimensional case, of the well-known Kolmogorov problem (2) on the kinetics of crystallization. For $n > 1$, the functions $f_n(t')$ can be determined tabularly by integrating (8). The integration should be carried out until two successive functions $f_n(t')$ and $f_{n+1}(t')$ satisfy condition (9) with the prescribed accuracy. To an accuracy of 0.01, fulfillment of the stationarity condition is achieved beginning with $n = 8$.

Fig. 1. Graphs of the functions $f_8(t')$ and $f_9(t')$

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In Fig. 1 the graphs of the functions $f_8(t')$ and $f_9(t')$ are shown. The quantity T is found as the difference of the arguments corresponding to one and the same value of the functions $f_n(t')$ and $f_{n+1}(t')$. The value obtained is $T = 0.63$. In addition, from condition (9) it is easy to see that T is expressed by the area enclosed between the graphs of the functions $f_n(t')$ and $f_{n+1}(t')$. Therefore we have the formula:

$$T = \int_0^\infty [f_n(t') - f_{n+1}(t')]\, dt'. \tag{11}$$

Verification by this formula gave the same value of T. The velocity of the normal advance of the crystallization front, which is the mean number of layers traversed by the front per unit time, is equal to $v = 1/T$, if time is measured in dimensionless units.

If the two-dimensional nuclei have the form of a regular polygon, the problem is solved analogously. The difference from the case considered is that the integration in (6) must be performed in the space of the variables x, y, τ over the volume of a certain pyramid. By changing the choice of the unit of time, the equation corresponding to equation (8) can be brought to the same form. Consequently, the functions $f_n(t')$ will have the same form as in the case of a disk-shaped nucleus, but on another time scale.

Novgorod State
Pedagogical Institute

Velikiye Luki State
Pedagogical Institute

Received
24 IV 1968

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2. A. N. Kolmogorov, Izv. AN SSSR, ser. matem., No. 3, 356 (1937).

Note: Figure translations are in progress. See original paper for figures.