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# Model of Mass Crystallization in Layers of Small Thickness

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The model of mass crystallization, which allows to take into account the blocking effect of the growing crystals by surfaces of thin layers of melt or rapidly quenched amorphous ribbons is proposed. The kinetic equations describing the contributions to the transformed volume fraction of the crystals which nucleate at considerable distances from the surfaces and maintain the initial spherical shape during whole solidification period, and those formed in the near-surface (critical) areas and undergoing the blocking effect of surfaces which results in the truncated sphere shape are derived. The analysis of the limiting versions of the model is performed. It is shown that using of the developed approach leads to reducing of the calculated values of the crystallized volume fraction up to 25%.

**Key words:** mass crystallization, thin layers, blocking crystals by surfaces, reducing of the transformed volume fraction.

## Introduction

In the numerical simulations and theoretical analysis of mass crystallization of melts and metallic glasses [1-6] the processes of homogeneous formation of spherical nucleus and their subsequent isotropic growth which are described by the equations of the classical theory of crystallization [7] are usually considered. In the approaches [1-3] based on the Kolmogorov-Johnson-Mehl-Avrami (KJMA) kinetic equation [8-10], deceleration of transformation due to impingement of the neighboring crystals is considered by means of a relation coupling the increments of the amounts of the real ($x$) and extended ($x^e$) transformed volume fractions:

$$dx = (1-x)dx^e \qquad (1)$$

In Refs. [4-6] this problem is solved within the frames of the effective rates of crystal nucleation ($I_{eff}$) and growth ($u_{eff}$) approach [11], according to which at a stage of mass crystallization increments of both volume density of crystallization centers ($dN$) and sizes of crystals ($dR$) for the elemental period ($dt$) are defined by the expressions:

$$dN = I_{eff}\,dt = (1-x)Idt \qquad (2)$$

$$dR = u_{eff}\,dt = (1-x)udt \qquad (3)$$

where $I$ and $u$ are the real rates of nucleation and growth of crystals, respectively.

It is necessary to note, that in all cited publications [1-6] the scheme in which the volume of an arbitrary grain is much smaller than the volume of the crystallizing system is considered. This scheme is valid for the traditional metallurgical production of metallic ingots and casts of large cross-sections. However, its using both for the melt quenching conditions and for heat treatment of rapidly quenched amorphous ribbons requires a special justification.

Really, in the mentioned processes the volume of a parent phase has a shape of the flat layer which thickness can be comparable to the sizes of nucleated crystals. It indicates that in analyzing of the crystal growth in thin layers it is necessary to consider not only inhibiting effect of neighboring centers which accounted by the classic model [8-10] and the approach [11], but also a possibility of size restriction of the crystals which in some current moment of a time reach the surfaces of the layer. To solve the specified problem the improved model of crystallization of layers of small thickness based on the relations (2) and (3) which allows to evaluate the relative contributions to the transformed volume fraction from the crystals forming in the central and near-surface areas of the layer is presented below.

## I. Physical assumptions of the model

Let us consider a layer of liquid or amorphous material with volume $V_0$ and thickness $l_0$, which is subjected to heat treatment in order to transform to a crystalline state. Assume that at some time moment $t_b$ the film begins to crystallize by homogeneous nucleation and isotropic growth. Consider, that crystalline nuclei can arise with equal probability in any point of a parent
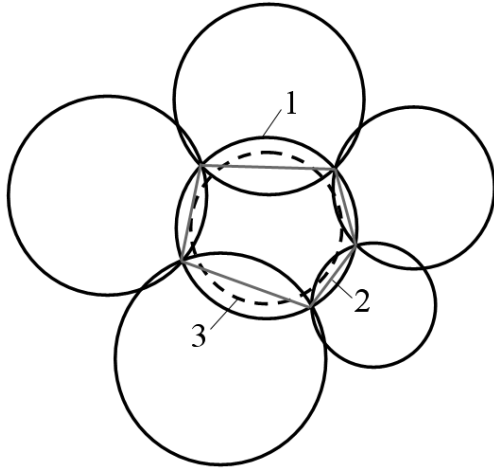
**Fig. 1.** Schematic presentation of interlocking crystals: 1 – model of free-growing crystals, 2 – model of crystals with polyhedral shape, 3 – model of a spherical crystal growing with effective rate $u_{\text{eff}}$.
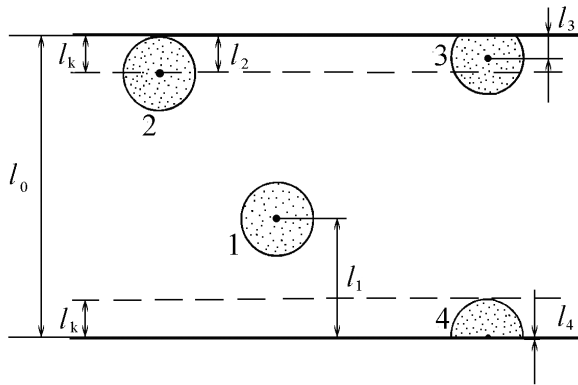


**Fig. 2.** To derivation of the kinetic crystallization equation of a thin layer: 1–4 –spherical crystals nucleated at the moment $t_b < t' < t_e$ at different distances $l_i$ from the surfaces of the film; $l_k$ is the width of the critical near-surface zones.

phase, including film surfaces. Assume also, that nuclei have the spherical shape which is inherited by crystals during their further growth with linear rate $u$ (model 1 on Fig. 1).

In fact, independent formation of individual crystals occurs only during the initial moments of transformation when the crystallized volume fraction is negligible. In time, with increasing of both a total number of crystallization centers and their sizes the probability of mutual impingements of neighboring crystals grows. In the contact areas of crystal the growth process stops, so that they acquire a polyhedral shape and reach smaller sizes than at free development (model 2 in Fig. 1).

Since impingements of crystals are random, the rigorous calculation of the final size and shape of the individual crystallites in the structure of the solidified metal is practically impossible. However, the main kinetic and morphological manifestations of these processes can be reproduced, assuming [11], that during the whole period of solidification the crystals retain a spherical shape, but grows with not physical, but with the effective rate $u_{\text{eff}} = (1-x)u$ ((model 3 in Fig. 1) which decreases with increase of $x$. This model of crystal growth at the stage of mass crystallization was used in the works [4-6].

The other factor limiting the free growth of crystals in a limited volume, is its interaction with the surfaces of the film. The blocking effect of the surfaces is experienced only a fraction of crystals, which increases with a rise of the total surface area to film volume ratio. Indeed, as schematically shown in Fig. 2, the crystals 1, 2 nucleated at $t = t'$ at large enough distances from the surfaces $l_i \,{}^3\, l_k$, at any later moment of time $t$ up to the end of the process $t_e$ hold the spherical shape. Therefore, the contribution of each of the crystals $V_1$ to the total transformed volume may be determined according to the formula for the volume of a sphere.

On the other hand, if the crystals arise in near-surface critical zones (crystals 3 and 4 in Fig. 2), at some time moments $t' \le t_i \le t$ they grow up to the nearest surface of the film, hereupon their growth in this direction stops. Quantitatively, this effect can be evaluated by setting a shape of truncated sphere to the crystals considered and the smaller final volume $V_2$ corresponding to this shape.

The width of the critical zone $l_k$ can be found from the condition that it is equal to the radius $R$ of the crystal, which nucleated at a moment $t'$ on the boundary (crystal 2 in Fig. 2) and then grows with effective rate $u_{\text{eff}}$ in time interval of $t'- t$:

$$l_k(t',t) = R(t',t) = R_k(t') + \int_{t'}^{t}(1-x(t''))u(t'')dt'' \qquad (4)$$

where $R_k$ is the critical radius of nucleus.

## II. Derivation of kinetic equation

According to the above considered principles of modeling, perform an analysis of the kinetics of mass crystallization in thin layers. Assume that at time $t'$ crystallized volume fraction is $x(t')$. Define the number of crystallization centers, which are formed in the parent phase during elementary interval $dt'$:

$$dN(t') = V_0(1-x(t'))I(t')dt' \qquad (5)$$

This total amount includes both nuclei arising away from the film surface $dN_1$, and the centers of nucleation formed in the critical near-surface zones $dN_2$. Because the nucleation processes are equally probable at all points of the film, the quantities $(dN_1)$ and $(dN_2)$ will be proportional to the relative volume of the central and near-surface zones, i.e.:

$$dN_1(t',t) = \left(1 - \frac{2l_k(t',t)}{l_0}\right)dN(t') \qquad (6)$$

$$dN_2(t',t) = \frac{2l_k(t',t)}{l_0}dN(t') \qquad (7)$$

Next define the contributions to the transformed volume from the crystals nucleated during the small

interval of time between $t'$ and $t'+dt'$ in two analyzed zones of the film:

$$dV_1(t',t) = V_1(t',t)dN_1(t',t) \qquad (8)$$

$$dV_2(t',t) = V_2(t',t)dN_2(t',t) \qquad (9)$$

In expressions (8) and (9) the parameters $V_1$ and $V_2$ represent the volume of full-sized and truncated spherical crystals growing at an effective rate in the time interval $t'-t$:

$$V_1(t',t) = \frac{4}{3}pR^3(t',t) \qquad (10)$$

$$V_2(t',t) = \frac{p}{3}(2R^3(t',t) + 3R^2(t',t)l_i(t',t) - l_i^3(t',t)) \qquad (11)$$

where $l_i(t',t)$ is the distance from the center of the crystals formed in critical areas to the film surface (Fig. 2).

Combining relations (5), (8) and (10) we obtain the kinetic equation, which allows to calculate the volume fraction of the film occupied by the spherical crystals of the central zone at any given time $t_b \le t \le t_e$:

$$x_1(t) = \frac{4}{3}p \int_{t_b}^{t} \left(1 - 2\frac{l_k(t',t)}{l_0}\right)(1-x(t'))I(t')R^3(t',t)dt' \qquad (12)$$

To obtain the corresponding dependence $x_2(t)$, describing the crystallization kinetics of critical near-surface zones of the film, it is necessary to determine the procedure for evaluation of the numerical values of the parameter $l_i(t',t)$ in formula (11) for the volume of a truncated sphere.

As can be seen from Fig. 2, the parameter $l_i(t',t)$ varies from 0 to $R(t',t)$, wherein, according to the proposed model, each act of the emergence of a new center of crystallization in the critical zone is related with some random value $0 \le l_i(t',t) < R(t',t)$, which can be selected using a Random Number Generator. To simplify the calculation algorithm we assume that instantaneous values $l_i(t',t)$ vary with time not randomly, but regularly,

for example, have a linear dependence of the form:

$$l_i(t',t) = R(t',t)(t'-t_b)/(t-t_b) \qquad (13)$$

According to relation (13) $l_i(t',t) \to 0$ when $t' \to t_b$. This means that at the initial moments of crystallization nuclei arise at the film surfaces. With time, the distance $l_i(t',t)$ increases from 0 to $R(t',t)$ at $t=t'$, which is equivalent to the nucleation horizons shifting from the surfaces to the boundaries of the critical zone.

Note that defined a priori ratio (13), as any other functional dependence $l_i(t',t)$, contradicts the principle used in the statistical model of nucleation and makes in this respect the proposed approach less physically rigorous. At the same time the development of crystallization in the critical areas of the film, described by equation (13), agrees with the idea of an easier nucleation of crystals at the contact places of the parent phase with the crystal surfaces, the role of which in this case can play the oxide film which occurring at the surfaces. In view of the above, equation (13) can be considered as a condition of spontaneous crystallization model adaptation to the features of heterogeneous nucleation mechanism, manifested in the border areas of the film.

In view of assumption (13) and expressions (11), (7) and (5) integration of the equation (9) gives the required relationship:

$$x_2(t) = \frac{2}{3}p \int_{t_b}^{t} \frac{l_k(t',t)}{l_0} A(t',t)(1-x(t'))I(t')R^3(t',t)dt' \qquad (14)$$

where

$$A(t',t) = 2 + 3(t'-t_b)/(t-t_b) - ((t'-t_b)/(t-t_b))^3 \qquad (15)$$

By summing the expressions (12) and (14) we find the total volume fraction of the film experience the transformation in period $t_b-t$:

$$x(t) = \frac{2}{3}p \int_{t_b}^{t} \left(2 + \frac{l_k(t',t)}{l_0}(A(t',t)-4)\right)(1-x(t'))I(t')R^3(t',t)dt' \qquad (16)$$

In equations (12), (14), (16), the parameter $R(t',t)$ is a radius of crystal nucleated at $t=t'$ and growing at a rate $u_{eff}$ until $t' \le t \le t_e$, which is calculated according to (4).

## III. Analysis of limiting versions of the kinetic equation

Equation (16) describes the mass crystallization kinetics in the layers with small thickness $l_0$, which is limited by two parallel surfaces. In contrast to the classical equation KJMA [8-10], derived for the case of large volume of the parent phase compared with those of the individual crystals, equation (16) takes into account the contributions to the total volume fraction transformed

$x(t)$ from the crystals formed in the inner part $x_1(t)$ and those nucleated in the near-surface critical areas $x_2(t)$. The relative value of these contributions depends on the ratio of the width of the critical areas $l_k(t',t)$ and the thickness of the melt $l_0$. Consider the limiting variants of the model by replacing in equation (16) the current values of variables $l_k(t',t)$ and $A(t',t)$ by their average values $\bar{l}_k$ and $\bar{A}$.

1. If the width of the critical areas is negligible compared with the film thickness of the melt $(\bar{l}_k/l_0 \to 0)$, then equation (16) takes the form:

$$x(t) \to x_V(t) = \frac{4}{3}p \int_{t_b}^{t} (1-x(t'))I(t')R^3(t',t)dt' \qquad (17)$$

where $x_V(t)$ is the transformed volume fraction, corresponding to a purely volume scheme of crystal formation.

In this case, crystals are not subjected to a blocking action of the surfaces and remain the spherical shape throughout the duration of the process.

The kinetic equation (17) obtained under these assumptions was used in the works [4-6] for modeling microstructure parameters of the melt quenching products. It has been shown that under the certain conditions of the rapid quenching the sizes of the formed crystals may exceed the thickness of the melt layer. This result of the numerical analysis served as the primary motivation for improving the thin layers crystallization model by taking into account the effect of blocking the growing crystal by film surfaces.

2. In another limiting case, when the total thickness of the critical areas is comparable with the thickness of the melt layer ($2\bar{l}_k \to l_0$), we get:

$$x(t) \to x_S(t) = \frac{p}{3} \int_{t_b}^{t} \bar{A}(1 - x(t'))I(t')R^3(t',t)dt' \quad (18)$$

where $x_S(t)$ is the transformed volume fraction of the film formed by crystals which are subjected to the blocking effect of the surfaces during growth.

It follows from the relations (15) that the numerical values of the parameter $A(t',t)$ during the the crystallization time interval $t_b$–$t$ vary from 2 to 4. Therefore, we can take $\bar{A} = 3$. Then for the ultimate version of the model under consideration, we obtain

$$x_S(t) = p \int_{t_b}^{t} (1 - x(t'))I(t')R^3(t',t)dt' \quad (19)$$

Comparison of equations (19) and (17) shows that, if all of the crystals are nucleated within the critical areas and therefore in further evolution take the shape of truncated spheres the total volume fraction $x_S(t)$ that has undergone transformation at time $t$ is less than the volume fraction, which crystallizes in the same time period $t_b$–$t$ in accordance with the mass crystallization process scheme which does not take into account interaction between the growing crystal and surfaces of the film.

The maximum relative decrease in the volume fraction crystallized due to the effect of blocking growing crystals by the parent phase layer surfaces $\left[x_V(t) - x_S(t)\right]/x_V(t)$ is 0.25. The resulting value is significantly higher than the errors in the experimental and theoretical estimates of the values $x(t)$ such indicating the appropriateness of the developed model using in studies of crystallization kinetics of layers with small thickness.

## Conclusions

The mass crystallization model, which takes into account the blocking effect of the growing crystals by surfaces of thin layers of melt or amorphous materials has been proposed. In the development of an effective approach rates of nucleation and crystal growth,

The kinetic equations describing the contributions to the transformed volume fraction of the spherical crystals formed in the central zone of the analyzed layers and those of the crystals nucleated in the near-surface critical areas which in accordance with the assumptions of the model, have the shape of a truncated sphere has been obtained.

Analysis of the limit variants of the model shows that neglecting of the effect of blocking layer of the growing crystal by surfaces of the film leads to an overestimation of the calculated values of the transformed volume fraction up to 25 %.

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Model of Mass Crystallization in Layers of Small Thickness

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# Модель масової кристалізації в шарах невеликої товщини

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Запропоновано модель масової кристалізації, яка дозволяє враховувати ефект блокування кристалів, що ростуть, поверхнями тонких шарів розплавів чи швидкозагартованих аморфних стрічок. Отримані кінетичні рівняння, які описують внески у частку перетвореного об'єму кристалів, що зароджуються на значних віддаленнях від поверхонь і зберігають протягом всього періоду твердіння вихідну сферичну форму, а також кристалів, що утворюються в приповерхневих критичних зонах, зазнають блокувальної дії поверхонь та набувають форму усіченої сфери. Виконано аналіз граничних варіантів моделі. Показано, що при використанні розробленого підходу розрахункові значення частки закристалізованого об'єму знижуються до 25 %.

**Ключові слова:** масова кристалізація, шари малої товщини, блокування кристалів поверхнями, зменшення частки перетвореного об'єму.