

UDC 532.8

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CRYSTALLIZATION KINETICS UNDER CONDITIONS OF THE QUENCHING FROM A LIQUID STATE

The model of bulk crystallization of the flat melt layers is presented. The model is based on the approach, according to which the processes of nucleation and crystal growth are carried out with effective rates proportional to the volume fraction of the parent phase. Contributions to the transformed volume fraction of x crystals nucleated at considerable distances from the surface of the film, and holding out initial spherical shape during the whole period of consolidation and also the crystals, arising on the near-surface critical areas that undergo the blocking effect of the surfaces and acquires the shape of truncated sphere are estimated in this model. The calculation analysis of crystallization kinetics of the $Fe_{80}B_{20}$ melt layers with thickness $l_o = 70 \mu m$, cooling on a massive copper heat receiver, is made with using the proposed model. It is shown that an increase in the critical areas of l_k relative volume occupied by truncated crystals increases, and at $l_k/l_o > 0,285$ their contribution to the overall share of the transformed volume becomes dominant.

Keywords: thin layers of melt, mass crystallization, the blocking effect of surfaces, spherical crystals, truncated crystals, contributions to the transformed volume fraction.

Представлена модель масової кристалізації плоских шарів розплаву малої товщини. Модель базується на приближенні, согласно которому процессы зарождения и роста кристаллов осуществляются с эффективными скоростями, пропорциональными объемной доле материнской фазы. В модели оцениваются вклады в долю превращенного объема x кристаллов, зарождающихся на значительных удалениях от поверхностей пленки и сохраняющих в течение всего периода затвердевания исходную сферическую форму, а также кристаллов, образующихся в приповерхностных критических зонах, которые испытывают блокирующее действие поверхностей и приобретают форму усеченной сферы. С использованием предложенной модели выполняется расчетный анализ кинетики кристаллизации слоев расплава $Fe_{80}B_{20}$ толщиной $l_o = 70 \mu m$, охлаждающихся на массивном медном теплоприемнике. Показано, что с ростом толщины критических зон l_k относительный объем, занятый усеченными кристаллами, возрастает и при $l_k/l_o > 0,285$ их вклад в общую долю превращенного объема становится доминирующим.

Ключевые слова: тонкие слои расплава, массовая кристаллизация, блокирующее действие поверхностей, сферические кристаллы, усеченные кристаллы, вклады в долю превращенного объема.

Наводиться модель масової кристалізації плоских шарів розплаву малої товщини, яка ґрунтується на наближенні, згідно з яким процеси зародження і росту кристалів здійснюються з ефективними швидкостями, пропорційними об'ємній частці материнської фази. У моделі оцінюються внески в частку перетвореного об'єму x кристалів, що зароджуються на значній відстані від поверхонь плівки і зберігають протягом усього періоду твердіння вихідну сферичну форму, а також кристалів, що утворюються у приповерхневих критичних зонах, які зазнають блокування поверхонь та набувають форми усеченої сфери. З використанням представленої моделі виконується розрахунковий аналіз кінетики кристалізації шарів розплаву $Fe_{80}B_{20}$ товщиною $l_o = 70 \mu m$, які охолоджуються на масивному мідному теплоприймачі. Показано, що з ростом товщини критичних зон l_k відносний об'єм, зайнятий усеченими кристаллами, зростає і при $l_k/l_o > 0.285$ їх внесок у загальну частку перетвореного об'єму стає доміантним.

Ключові слова: тонкі шари розплаву, масова кристалізація, блокуюча дія поверхонь, сферичні кристали, усечені кристали, внески в частку перетвореного об'єму.

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Introduction

The classical theory of mass crystallization is based on the kinetic equation of Kolmogorov [1] obtained under the assumption that the linear dimensions of individual crystals is incomparably smaller than the characteristic size of crystallized volume. This assumption is valid for the traditional metallurgical production processes of metal ingots and castings of large cross-sections. However, it does not hold under the conditions of quenching from the liquid state when the melt takes the form of a flat layer, the thickness of which is comparable with the size of the formed crystals. It is obvious that in this case the analysis of the crystal growth processes one should be taken into account not only the retarding action of neighboring particles, which is provided both by the classical model [1] and by the model based on the approximation of effective rates of crystal nucleation and growth [2–4], but also the possibility of the limiting size of those crystals that during the consolidation reach the layer surface has to be analyzed.

To solve the specified problem with developing the model [2], an improved model of crystallization of thin layers of melt is presented in the present paper, which allows evaluating the contributions to the transformed volume fraction of the two types of crystals forming in the central and near-surface areas of the layer. The calculation analysis of the mass crystallization kinetics of the $\text{Fe}_{80}\text{B}_{20}$ melt layers of $70\ \mu\text{m}$ thickness cooled by a massive copper substrate is made with the proposed model use.

Statement of the problem

Let us consider a liquid metal film of volume V_o and thickness l_o , which is cooled rapidly by the heat removing to the substrate (Fig. 1). Let us assume that by the time t_m the melt achieves the melting temperature T_m , the regular cooling mode is set in the film [5], and the whole volume simultaneously goes into the supercooled state.

At temperatures $T < T_m$ the film starts crystallizing by homogeneous nucleation and the further isotropic growth of the formed crystals. In the simplest version of the model we shall assume that the points lying within the melt volume and its surface are equivalent in their crystal-nucleating ability, i.e. at all points including surface ones a single mechanism of spontaneous nucleation operates.

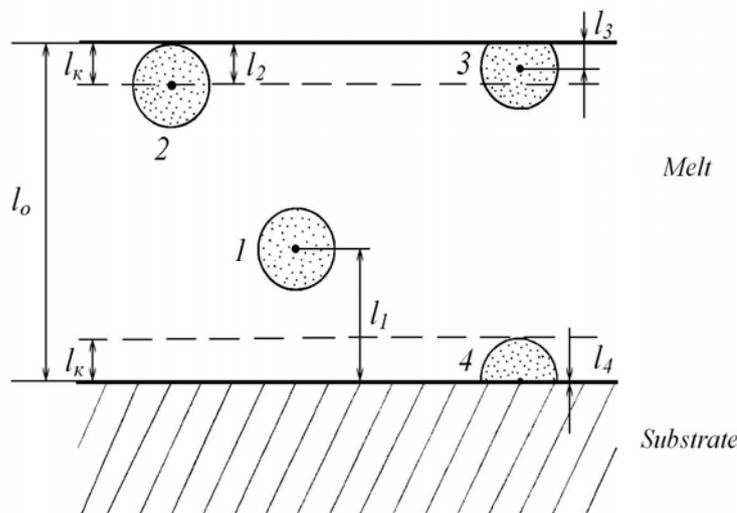


Fig. 1. Derivation of the kinetic crystallization equation of a thin melt layer that is cooled on the heat conductive substrate: 1 - 4 – hypothetical spherical crystals nucleated at a moment $t_m < t' < t_e$ at different distances l_i from the surfaces of the film; l_k – width of the critical near-surface zones.

Under such conditions of rapid quenching the transformation occurs in the temperature range from T_m to a final value T_e when the crystallized mass growth stops because of the complete exhaustion of the liquid phase or due to the material transition into the solid amorphous state. In the latter case the temperature T_e takes the sense of the glass transition temperature T_g . In the time scale the crystallization process takes a range of $t_m - t_e$.

Let us assume that the nuclei have a spherical shape inherited by crystals in their free growth at an effective rate:

$$u_{eff} = (1 - x)u \quad (1)$$

where x is the volume fraction which has undergone transformation; u is the real rate of crystal growth.

As shown in [2] by means of the approximation (1), the processes of the crystallization retarding through mutual collisions of neighboring crystals can be modeled.

The other factor limiting the free growth of crystals in a restricted volume is their interaction with the film surfaces. The blocking effect of the surfaces is experienced only by the fraction of crystals increasing with the growth ratio of the total surface area to film volume. Indeed, as schematically shown in the Fig. 1, the crystals nucleated at $t = t'$ at large enough distances from the surfaces $l_i \geq l_K$ (crystals 1, 2 in Fig. 1) hold the shape of spherical particles at any specified time $t' \leq t \leq t_e$. Therefore, the contribution of each crystal $V_1(t', t)$ to the total volume subjected to the conversion may be determined according to the formula for the volume of a sphere:

$$V_1(t', t) = \frac{4}{3} \pi R^3(t', t) \quad (2)$$

where $R(t', t)$ is a radius for a crystal nucleated at the moment t' and growing till the moment t with the effective rate u_{eff} .

It is obvious, that

$$R(t', t) = R_K(t') + \int_{t'}^t (1 - x(t'')) u(t'') dt'' \quad (3)$$

where R_K is a radius of critical nucleus; $t' \leq t'' \leq t$.

On the other part, if crystals arise in near-surface critical zones (crystals 3, 4 in Fig. 1), at some time moments $t' \leq t_i \leq t$ they grow up to the nearest surface of the film that prevents their further growth in this zone. Quantitatively, this effect can be evaluated through setting to the considered crystals a truncated sphere form corresponding to the shape of the smaller final volume V_2

$$V_2(t', t) = \frac{\pi}{3} (2R^3(t', t) + 3R^2(t', t) \cdot l_i(t', t) - l_i^3(t', t)) \quad (4)$$

where $l_i(t', t)$ is a distance from the centre of a crystal forming in the critical zones to the blocking film surface.

The width of the critical zones can be found from the condition that it is equal to the radius R_e of crystals nucleated at a moment t' on their boundaries (crystal 2 in Fig. 1) and then growing isotropically in interval $t' - t$ according to Eq. (3), i.e.

$$l_K(t', t) = R(t', t). \quad (5)$$

Derivation of kinetic equation

On the basis of the above considered principles of modeling, we can derive the kinetic equation taking into account the specifics of crystallization processes in thin layers.

Let us suppose that at time $t_m \leq t' \leq t_e$ a crystallized volume fraction is $x(t')$ and determine the number of critical size nuclei $R_K(t')$ arising in the areas of location of the parent phase for a small period of time between t' and $t'+dt'$

$$dN(t') = V_0(1 - x(t'))I(t')dt' \quad (6)$$

where $I(t')$ is a frequency of nucleation per volume unit in the parent phase.

This total amount includes both nuclei arising away from the surface (dN_1) and ones with nucleation centers in the critical near-surface zones (dN_2). So far as by hypothesis the nucleation processes are equiprobable at all points of the melt layer, the quantities (dN_1) and (dN_2) will be proportional to the relative volume of the considered parts of the film, i.e.

$$dN_1(t', t) = \left(1 - \frac{2l_K(t', t)}{l_0}\right) dN(t'), \quad (7)$$

$$dN_2(t', t) = \frac{2l_K(t', t)}{l_0} dN(t'). \quad (8)$$

Further we define the value of the crystallizing volume increment provided by crystals nucleated within a specified short time interval in two zones of the film:

$$dV_1(t', t) = V_1(t', t)dN_1(t', t), \quad (9)$$

$$dV_2(t', t) = V_2(t', t)dN_2(t', t). \quad (10)$$

As follows from Fig. 1, the parameter $l_i(t', t)$ involved to Eq. (4) varies from 0 to $R(t', t)$, wherein, according to the model used, each act of the new center of crystallization forming in the critical zone is connected with one of the values of $l_i(t', t)$ from the current interval. For simplicity of choice procedure of possible critical distances $l_i(t', t)$ we assume that they change with time according to linear dependence in the form:

$$l_i(t', t) = R(t', t) \cdot (t' - t_m) / (t - t_m). \quad (11)$$

This means, that at the initial moments of crystallization ($t' \rightarrow t_m$) $l_i(t', t) \rightarrow 0$, i.e. nuclei arise at the film surface. With the course of time, the distance $l_i(t', t)$ increases from 0 to $R(t', t)$. It is equivalent to the shift of the layer, where the centers of crystallization arise from the surface to the boundary of the critical zone.

Specification of the dependence behavior $l_i(t', t)$ allows us to calculate the values $dV_1(t', t)$ and $dV_2(t', t)$ and by means of them the film volume fractions formed by the crystals of the central ($x_1(t)$) and adjacent to surfaces ($x_2(t)$) zones at any defined time moment $t_m \leq t \leq t_e$:

$$x_1(t) = \frac{4}{3} \pi \int_{t_m}^t \left(1 - 2 \frac{l_K(t', t)}{l_0}\right) (1 - x(t')) \cdot I(t') \cdot R^3(t', t) dt', \quad (12)$$

$$x_2(t) = \frac{2}{3} \pi \int_{t_m}^t \left(\frac{l_k(t',t)}{l_o} \right) \cdot A(t',t) \cdot (1-x(t')) \cdot I(t') \cdot R^3(t',t) dt' \quad (13)$$

$$\text{where} \quad A(t',t) = 2 + 3(t' - t_m)/(t - t_m) - ((t' - t_m)/(t - t_m))^3. \quad (14)$$

By summing the values $x_1(t)$ and $x_2(t)$ with taking into account Eq. (3) we obtain the total volume fraction of the crystalline phase:

$$x(t) = \frac{2}{3} \pi \int_{t_m}^t \left(2 + \frac{l_k(t',t)}{l_o} (A(t',t) - 4) \right) (1-x(t')) \cdot I(t') \cdot \left(R_k(t') + \int_{t'}^t (1-x(t'')) u(t'') dt'' \right)^3 dt' \quad (15)$$

The results of model calculations

Eq. (15) describes the kinetics of crystallization in the molten layers of small thickness l_o bounded by two lengthy parallel surfaces. In contrast to the well-known Kolmogorov equation [1] derived concerning the strictly volumetric scheme of the crystallization, Eq. (15) allows to take into account the contributions to the total crystallized volume fraction x of two parts made by crystals emerging away from the film surface (x_1) and in the crystal in the near-surface zones (x_2). As seen from Eqs. (12) and (13), the magnitude of these contributions depends on the ratio of the the critical bands width l_K and the layer thickness l_o .

In order to analyze these dependencies in more detail the equations (12), (13) and (15) were solved concordantly with the equations for heat conduction of the melt layers $\text{Fe}_{80}\text{B}_{20}$ of $l_o = 70 \mu\text{m}$ thickness subjected to the cooling on the copper quenching block. The calculations were performed by the numerical method of finite differences using explicit difference scheme [6]. Temperature rate dependences of the nucleation and crystal growth as well as the values used in the calculations of thermal variables were taken from the paper [7]. Parameter A was taken to be equal to its average value of 3. The width of the critical areas l_K was assumed to be independent of time. In different series of calculations we used fixed values l_K that belonged to the interval $0 - 0.5l_o$.

Fig. 2 shows the estimated dependences $x_1(t)$, $x_2(t)$ and $x(t)$, corresponding to the two values of the ratio l_K/l_o . As can be seen from the figure, the characteristic feature of the obtained kinetic curves is a sharp change in slope at some time t_s . The analysis of the full array of calculated data shows that during the passage of the inflection point the temperature of the crystallizing layer increases abruptly, verge towards the T_m ; the frequency of nucleation falls almost to zero, and the crystal growth rate value remains high enough ($u(t_s) \approx 1.4 \text{ m/s}$). This leads to the conclusion that the crystallization process is carried out in two stages. At the first stage (at $t < t_s$) the transformation arises at significant supercooling of the melt by the nucleation of new crystals and their further growth. At the point t_s an intensive release of the latent heat of crystallization occurs, the primary supercooling is removed, whereupon the formation of new nuclei is stopped and the further volume fraction increase of the crystalline phase arises only owing to the growth of previously nucleated crystals.

As follows from the comparison of Figs. 2a and 2b, the relative contributions to the value x of the two crystal types considered in the model depend on the value of ratio l_K/l_o . Thus, in the films with relatively small width of the critical zones ($l_K/l_o = 0.1$), crystals preserving the original spherical shape are mainly involved in the conversion (Fig. 2a).

For this example the final (at $t = t_e$) value x_1^e is 0.83. With the increase in the ratio l_K/l_o the growing contribution to the total volume fraction of the crystalline phase is made by crystals that at a certain stage of the process reach the surface of the melt film and, in accordance with the proposed model, take the form of truncated sphere. In particular, at $l_K/l_o = 0.4$ $x_2^e = 0.74$ (Fig. 2b).

In summary, the dependence of values x_1^e and x_2^e on the specific width of the critical areas l_K/l_o are shown in Fig. 3. It is evident, that in the range $l_K/l_o = 0-0.5$ the resulting truncated crystal volume fraction increases from 0 to 1, and the relative amount of full-sized spherical crystals is reduced accordingly. If $l_K/l_o = 0.285$, the equality of the values x_1^e and x_2^e is reached, i. e. both types of crystals make equal contributions to x^e .

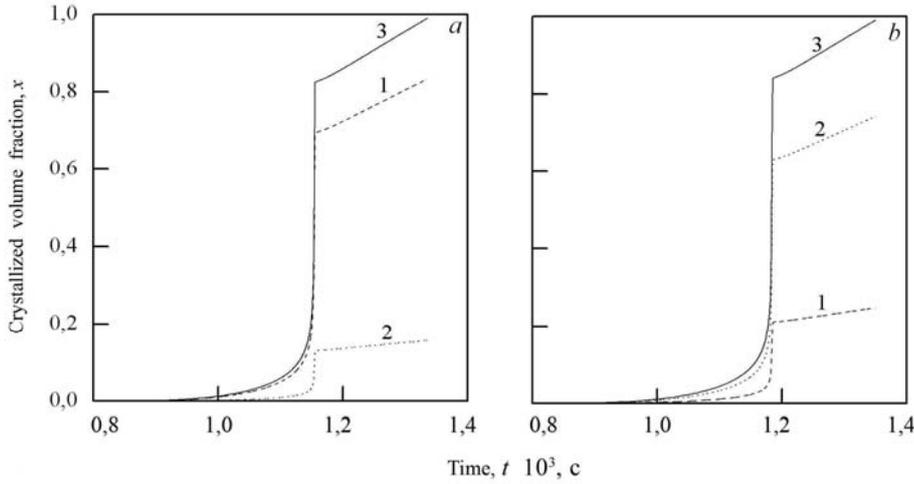


Fig. 2. Time dependences graphs of the crystalline phase amount for foils of $l_o = 70 \mu\text{m}$ thickness at $l_K = 0,1l_o$ (a) and $l_K = 0,4l_o$ (b): 1 - fraction of the crystalline phase made by a spherical crystals x_1 ; 2 - fraction of the crystalline phase made by truncated crystals x_2 ; 3 - the total fraction of the crystalline phase x

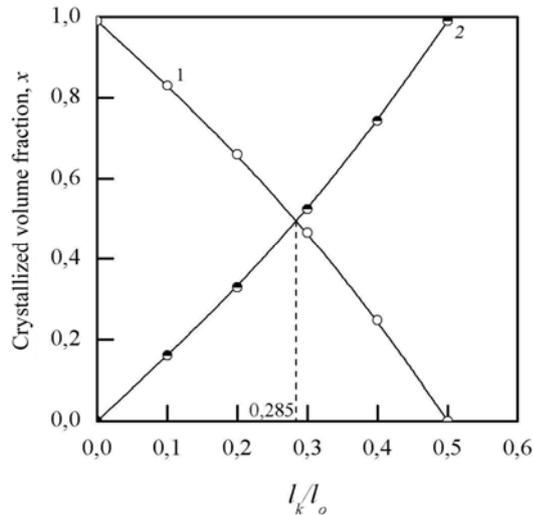


Fig. 3. The dependence of the crystalline phase fraction of the critical bands width l_K : 1 - the fraction of spherical crystals x_1 ; 2 - the volume fraction of crystals of a truncated form x_2

Conclusions

In the context of the approximation of effective rates of nucleation and crystal growth an improved model of mass crystallization of thin layers of melt, which takes into account the blocking effect of the growing crystals surfaces of the film has been created.

Kinetic equations for the processes of formation of spherical crystals nucleated away from the surface layer and crystals formed in the surface of the critical areas that undergo the blocking effect of surfaces and acquires the shape of truncated sphere have been derived.

The calculation analysis of crystallization kinetics of the $\text{Fe}_{80}\text{B}_{20}$ melt layers with thickness $l_0 = 70 \mu\text{m}$ cooled on a massive copper heat absorber has been made using the supposed model. It has been shown that with the increase in the width of the critical areas l_K the relative amount of truncated crystal grows and at $l_K/l_0 = 0.285$ their contribution to the overall fraction of the transformed volume becomes dominant.

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Received 13.07.2013.