Exact solution of the problem of dissolved gas segregation by the plane crystallization front

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Abstract. Analytical solution of the segregation problem was found for the arbitrary crystal growth law using the quasi-steady-state approximation. The segregation is caused by the displacement of dissolved gas by moving plane crystallization front. The effect of solidification shrinkage on the crystallization process was taken into account. It is shown that in the case of “equilibrium crystallization” (when the growth rate is in inverse ratio to time) the solution of the problem becomes self-similar. In this case gas concentration at the crystallization front stays the same during the whole process while the diffusion layer thickness increases with time.

1. Introduction

The major part of modern materials are being created by the way of solidification from melts. Depending on the conditions one can create various forms of solid matter: crystalline, amorphous, clathrate compound and others [1–6]. All processing technologies of producing solid materials are in one form or another associated with minimizing or eliminating two factors: shrinkage and gas porosity. Thus, creating fully consistent theory allowing to account for these seems to be the relevant task.

Ultra-rapid quenching from melt causes extreme cooling rates allowing to transfer the melt into deeply metastable state. Under such conditions the melt solidification is a result of fluctuation nucleation and the growth of new phase nuclei [1, 7]. It is noted in a number of articles on the experimental research of such a processes that the micropores and cracks in solidified material can be caused by the shrinkage of substance in solidification process [8–12]. In [13] it is shown that the formation of even a small fraction of crystal phase leads to significant tension stress in uncrystallized melt which leads to intensive cavitation. The results show that the size of crystal grains and cavities in solidified material depend very heavily on the rate of melt cooling.

Another mechanism of pore formation during crystallization of gas-saturated melts is the gas segregation in the process of crystallization [14]. The solubility of gas in the solid is substantially less than solubility of gas in the liquid, so the gas dissolved in the melt will be forced out by the moving crystallization fronts. As a result the gas will “accumulate” near the phase transition front. At the moment when gas concentration exceeds the critical one (corresponding to gas solubility in the melt under given conditions) nucleation and growth of gas bubbles occur. Further on crystallization front captures bubbles and the solidified material has a porous structure as a result. Number of articles are devoted to this problem [15–21]. Alas, the majority of them are
dealing with the case of low crystal growth rate and take no account for the shrinkage of the substance.

2. Statement of the problem

Let us consider the problem of segregation of gas dissolved in the melt caused by moving crystallization front in the case of plane crystallization.

The dependence of dissolved gas concentration field on time during crystallization is described by the diffusion equation:

$$\frac{\partial C}{\partial t} + v_l \frac{\partial C}{\partial x} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right),$$  \hspace{1cm} (1)

where $t$ — time; $x$ — the coordinate with the origin at the crystallization center; $C$ — mass fraction of the gas dissolved in the melt; $D$ — diffusion coefficient for the gas in the melt.

Let us note that eq. (1) has a convective term caused by the shrinkage of the melt during solidification. For incompressible liquid: $v_l = -k \dot{X}$. Where $X$ — coordinate of crystallization front (initially $X = 0$); $k = \rho_s/\rho_l - 1$ — shrinkage coefficient; $\rho_s$ and $\rho_l$ — densities of solid and liquid phases respectively.

The dependence of the coordinate of crystallization front $X$ is obtained by solving the problem of crystal growth in supercooled melt. Without getting into specifics let us note that the crystallization processes can be divided into two categories [2,22,23]: non-equilibrium and equilibrium ones.

We will assume that initially the dissolved gas concentration in the melt is homogeneous and equal to $C_0$:

$$\left(C\right)_{t=0} = C_0,$$ \hspace{1cm} (2)

moreover $C_s < C_0 < C_l$, where $C_s$ and $C_l$ — solubility of gas in solid phase and solubility in liquid phase respectively.

Boundary conditions consist of following. At large distance from the crystal concentration of dissolved gas is equal to initial one:

$$\left(C\right)_{x \to \infty} = C_0;$$ \hspace{1cm} (3)

Material balance equation hold true at the interphase:

$$\rho_l \left(C\right)_{x=X} \left( dX + kdX \right) = \rho_s C_s dX - \rho_l D \left( \frac{\partial C}{\partial x} \right)_{x=X} dt,$$

or

$$-D \left( \frac{\partial C}{\partial x} \right)_{x=X} = (1 + k) \dot{X} \left\{ \left(C\right)_{x=X} - C_s \right\}.$$ \hspace{1cm} (4)

Boundary problem (1)–(4) fully describes the segregation process during crystallization. Introducing following non-dimensional variables: \(\tilde{C} = \frac{C - C_0}{C_0 - C_s}; \tau = t/t_0; \tilde{x} = x/x_0; \tilde{X} = X/x_0; \dot{\tilde{X}} = d\tilde{X}/d\tau = \tilde{X}/v_0; \chi = \tilde{x}/\tilde{X}\), where $t_0 = D/v_0^2$ and $x_0 = D/v_0$ — characteristic time of the process and characteristic size respectively. As a characteristic velocity of the process $v_0$ we will use the characteristic growth rate of the crystal.

By using the variables $\tau$ and $\chi$ we transform the boundary value problem (1)–(4) into the problem with fixed boundaries. Similar approach was also used in [23,24]. Using these new variables we can transform the problem to the following form:

— diffusion equation:

$$\frac{\partial \tilde{C}}{\partial \tau} = \frac{\dot{\tilde{X}}}{\tilde{X}} \left( k + \chi \right) \frac{\partial \tilde{C}}{\partial \chi} + \frac{1}{\tilde{X}^2} \frac{\partial^2 \tilde{C}}{\partial \chi^2},$$ \hspace{1cm} (5)
initial condition and boundary conditions:

$$(C)_{\chi \to \infty} = 0; \quad - \left( \frac{\partial C}{\partial \chi} \right)_{\chi=1} = (1 + k) \tilde{X} \tilde{X} \left\{ (C)_{\chi=1} + 1 \right\}.$$  \hspace{1cm} (6)

This boundary problem in the general form can only be solved numerically. But, considering that the concentration of dissolved gas in the process of crystallization is a slowly varying function of time we can assume $\partial C / \partial \tau \approx 0$. It will be shown below that this assumption allows us to obtain the quasi-stationary solution of the problem. It is in good agreement with the numerical solution and in the case of equilibrium crystallization represent the exact solution.

3. Analytical solution of the problem

Integrating the diffusion equation (5) and using boundary conditions the quasi-stationary solution of the problem for plane crystallization front can be found:

$$\tilde{C}(\tau, \chi) = \tilde{C}(\tau, 1) \frac{\text{erfc}\left\{ \sqrt{\tilde{X} \tilde{X}} / 2 \ (\chi + k) \right\}}{\text{erfc}\left\{ \sqrt{\tilde{X} \tilde{X}} / 2 (1 + k) \right\}}.$$ \hspace{1cm} (7)

where $\tilde{C}(\tau, 1)$ — gas concentration at the crystallization front. It is a sought-for function and can be found from the material balance equation (6):

$$\tilde{C}(\tau, 1) = \frac{\sqrt{\pi}(1 + k) \sqrt{\tilde{X} \tilde{X}} / 2 \ \text{erfc}\left\{ (1 + k) \sqrt{\tilde{X} \tilde{X}} / 2 \right\}}{\exp\left\{ -(1 + k)^2 \tilde{X} \tilde{X} / 2 \right\} - \sqrt{\pi}(1 + k) \sqrt{\tilde{X} \tilde{X}} / 2 \ \text{erfc}\left\{ (1 + k) \sqrt{\tilde{X} \tilde{X}} / 2 \right\}}.$$ \hspace{1cm} (8)

In the case of equilibrium crystallization of the melt the function $\tilde{X} \tilde{X} = 2 \beta^2 = \text{const}$. It means that the concentration field in this case is stationary. Thus, the solution of the boundary problem becomes a self-similar one (with self-similar variable $\chi$) and the exact one at that because no approximations were used to obtain it:

$$\tilde{C}(\chi) = \frac{\sqrt{\pi} \beta (1 + k) \ \text{erfc}\left\{ \beta (\chi + k) \right\}}{\exp\left\{ -\beta^2 (1 + k)^2 \right\} - \sqrt{\pi} \beta (1 + k) \ \text{erfc}\left\{ \beta (1 + k) \right\}}.$$ \hspace{1cm} (9)

In the case of no shrinkage ($k = 0$) similar solution was obtained in [14] using different technique.

For the cases of small and big values of the parameter $\beta$ following asymptotic approximations can be found.

For $\beta \ll 1$ (close to the crystallization front):

$$\tilde{C}(\chi) \approx \tilde{C}(1) \left\{ 1 - (2\beta / \sqrt{\pi}) (\chi - 1) \right\}, \quad \tilde{C}(1) \approx \sqrt{\pi} \beta (1 + k);$$ \hspace{1cm} (10)

For $\beta \gg 1$:

$$\tilde{C}(\chi) \approx \tilde{C}(1) \frac{1 + k}{\chi + k} e^{-\beta^2 \{ (\chi+k)^2 -(1+k)^2 \}}, \quad \tilde{C}(1) \approx 2\beta^2 (1 + k)^2 + 2;$$ \hspace{1cm} (11)
4. Conclusions
The problem of dissolved gas segregation in melt by the plane crystallization front is formulated taking account of the solidification shrinkage. Analytical solution of the problem was found using the quasi-steady-state approximation. The solution is applicable for the arbitrary crystal growth law (the obtained approximate solution shows good fit with the exact solutions for extreme cases). It is found that in the case of “equilibrium crystallization” (when the growth rate is in inverse ratio to the square root of time) the solution of the problem becomes self-similar and exact. In this case gas concentration at the crystallization front instantly increases and stays at the value that depends on the crystal growth rate. At the same time the diffusion layer thickness increases proportionally to the square root of time. The effect of solidification shrinkage on the process at hand is shown.

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