Gas segregation during crystallization process

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A B S T R A C T

Analytical solution of the problem of dissolved gas segregation from melt during the crystallization process was found. The problem was solved using 3 most commonly used geometries of crystal growth: plane, cylindrical and spherical. Shrinkage of the melt during crystallization was correctly taken into account. It was shown that in the case of equilibrium crystallization the solution becomes self-similar. The criteria allowing to predict the conditions for inevitable formation of cavities in solidified material is shown.

1. Introduction

It is common knowledge that the bulk of modern materials are being created by the way of crystallization from melts. Not focusing on powder metallurgy and a couple of other technologies the main method consists of melting, homogenization, and subsequent solidification. The technologies based on the method of ultra-rapid quenching from melt (technologies of plasma flame spraying, melt spinning, etc.) stand out against all others. Key feature of the method is rapid transition of melt into metastable state and subsequent intensive phase transition. It allows the production of a variety of promising materials with unique physicochemical properties widely used in modern engineering, microelectronics, medicine, etc. Such materials can be amorphous, nanocrystalline and bioactive. The properties of such materials directly depend on their morphology so the ability to control it is the key to production of materials with specified functional characteristics. Here, 2 factors play the roles of no small importance - effects of shrinkage, and gas porosity. All processing technologies of producing solid materials are in one form or another associated with minimizing or eliminating this two factors. Thus, creating fully consistent theory allowing to do it (and in non-equilibrium condition at that) seems to be the relevant task.

As mentioned before, 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 [1,2]. 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 [3–7]. In [8] 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 [9]. 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 [10–16]. Alas, the majority of them are dealing with the case of equilibrium successive crystallization (plane crystallization front) with low crystal growth rate and take no account for the shrinkage of the substance. This work is an effort to fill some existing gaps. Namely, the work is aimed at solving the problem of segregation of gas dissolved in the melt in three different geometries of crystallization front using arbitrary crystal growth law and taking the shrinkage of the substance in the process of solidification into account.

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Nomenclature

a	thermal conductivity of the melt, m^2/s
c	specific heat capacity, J/(kg·K)
C	concentration of gas dissolved in melt, kg/kg
C_l	solubility of gas in liquid phase, kg/kg
C_s	solubility of gas in solid phase, kg/kg
C_0	initial concentration of gas dissolved in melt, kg/kg
$\overline{C} = (C - C_0)/(C_0 - C_s)$	dimensionless concentration
D	diffusion coefficient, m^2/s
$k = \rho_s/\rho_l - 1$	shrinkage coefficient
Ku $= L/(c\Delta T_0)$	Kutateladze number
L	specific heat of phase change, J/kg
Le $= D/a$	Lewis number
t	time, s
$t_0 = D/v_0^2$	characteristic time, s
ΔT_0	melt supercooling, K
v_0	characteristic rate of the crystal growth, m/s
$v_r = -k\dot{X}(X/x)^{\alpha}$	radial velocity of liquid, m/s
x	the coordinate with the origin at the crystallization center, m
$x_0 = D/v_0$	characteristic dimension of the process, m
X	the coordinate of crystallization front, m

Greek symbols

α	coefficient corresponding to the geometry of the problem
β	dimensionless coefficient
β_D	dimensionless coefficient
β_T	dimensionless coefficient
$\delta = x - X$	coordinate relative to the crystallization front, m
δ_D	thickness of diffusive boundary layer, m
$\overline{\delta} = (\chi - 1)\overline{X}$	dimensionless coordinate relative to the crystallization front
ζ	dimensionless integration variable
ρ	density, kg/m^3
$\tau = v_0^2 t/D$	dimensionless time (Fourier number)
$\chi = \bar{x}/\overline{X}$	dimensionless coordinate
χ_D	dimensionless thickness of diffusive boundary layer

Subscripts

l	liquid phase
s	solid phase
"0"	characteristic value

2. Statement of the problem

Let us consider the problem of segregation of gas dissolved in the melt caused by moving crystallization front (schematically this process is depicted in Fig. 1) for three most common geometries:

- Plane crystallization front, when the nucleation of the crystal occurs on the plane heterogeneous surface (substrate). Usually the heat can be removed through substrate.
- Cylindrical crystallization front, when the nucleation of the crystal occurs on filamentary primer.
- Spherical crystallization front, when the nucleation of the crystal occurs inside the volume of the melt on submicron primer or homogeneously.

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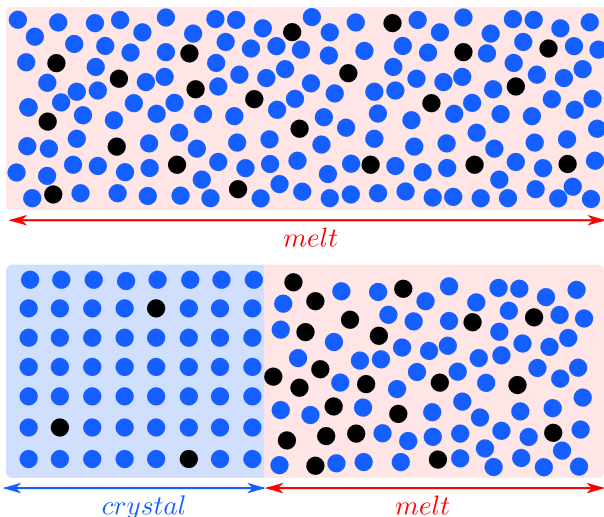

Fig. 1. Schematic depiction of dissolved gas segregation in the process of crystallization (black circles represent dissolved gas molecules).

can be given in the form that accounts for all three different geometries under study:

$$\frac{\partial C}{\partial t} + v_l \frac{\partial C}{\partial x} = \frac{1}{x^{\alpha}} \frac{\partial}{\partial x}\left(Dx^{\alpha}\frac{\partial C}{\partial x}\right), \tag{1}$$

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. Hereinafter we assume all of the thermophysical properties to be constant during the process. Values of the coefficient $\alpha = 0$; 1 and 2 correspond to plane, cylindrical and spherical symmetries respectively.

Let us note that Eq. (1) has a convective term caused by the shrinkage of the melt during solidification. The shrinkage draws the liquid towards the interphase (in the case when the density of solid phase is greater than the density of liquid phase). The velocity of the melt v_l can be found from the continuity equation. For incompressible liquid: $v_l = -k\dot{X}(X/x)^{\alpha}$. Where X — coordinate of crystallization front (initially $X = 0$); $\dot{X} = dX/dt$ — the crystal growth rate; $k = \rho_s/\rho_l - 1$ — shrinkage coefficient; ρ_s and ρ_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. In the model we believe that the diffusion process does not affect the crystallization process. Without getting into specifics let us note that the crystallization processes can be divided into two categories [17–19]. First type — non-equilibrium crystallization, when the crystal growth rate is defined by the kinetics of phase transition and depend on supercooling of the melt on the crystallization front. If the supercooling stays constant during the whole process, so the growth rate stays constant: $\dot{X} = v_0 = \text{const}$; $X = v_0 t$. Second type — equilibrium crystallization, when the growth rate is defined only by the heat transfer from the interphase (supercooling of the melt at the crystallization front is close to zero). In this case the crystal growth rate is in inverse proportion to square root of time: $\dot{X} = \beta_T \sqrt{a/t}$; $X(t) = 2\beta_T \sqrt{at}$, where $\beta_T = \beta_T(\mathbf{Ku})$ — non-dimensional coefficient representing the function of Kutateladze number $\mathbf{Ku} = L/(c\Delta T_0)$; L — specific heat of phase change; c — specific heat capacity; a — thermal conductivity of the melt. Certainly, real crystallization processes obey more