PERGAMON

International Journal of Heat and Mass Transfer 46 (2003) 915–919

International Journal of
HEAT and MASS TRANSFER

www.elsevier.com/locate/ijhmt

Exact solution of the problem of gas segregation in the process of crystallization

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Received 17 January 2002

Abstract

In the present work, we theoretically investigate the problem of gas segregation in the process of crystallization. The self-similar solutions of the problem for a flat and spherical solidification fronts moving with the velocity inversely proportional to the square root of time are found. The criteria of the elimination of gassing due to segregation are proposed. Using the Laplace transformation method, an analytical solution of the problem for a flat solidification front moving with a constant velocity is also obtained.

1. Introduction

It is known that in some cases the process of crystallization is accompanied by gas liberation which leads to the formation, in a solid phase, of the pores which substantially influence the properties of the material obtained. The reason for this phenomenon is that the solubility of a gas in a solid phase C_s is substantially smaller than that in a liquid one C_{liq}. Therefore, if the initial concentration of the gas dissolved in a melt $C_0 > C_s$, the gas which cannot be captured by the solid phase will be displaced in the process of solidification by the moving crystallization front. In [1], a numerical solution of the problem of gas segregation by a moving plane front of phase transition is given.

At the time, when the gas concentration at the crystallization front exceeds the critical one, the formation of gas bubbles begins. At small crystallization rates they are formed predominantly on the surface of a growing crystal [2]. At large crystallization rates, a volumetric mechanism of gas evolution is also possible.

Thereafter, the formed bubbles are captured by the solid phase [3,4]. At small crystallization rates a captured bubble preserves its contact with the liquid phase and remains to be a sink for the gas evolved. As a result, columnar gas inclusions are formed in the solid phase [5]. The mean degree of the elongation of the captured inclusions decreases with increase in the rate of crystallization and their density grows. Beginning with the crystallization rates exceeding 3.5×10^{-3} cm/s, the shape of the inclusions captured is close to a spherical one. We note that under actual regimes of solidification of metal melts and, the more so, in solidification of thin specimens, the crystallization rate are an order of magnitude higher than this value.

We note that since in the majority of metals and alloys the density of the solid phase is higher than of the liquid one, a cavitation mechanism of the formation of gas cavities is also possible in the case of spontaneous crystallization. This problem requires thorough investigation and this is the aim of our further investigations.

In the present work we have found self-similar solutions of the problem of displacement of the gas dissolved in a melt by a plane and a spherical crystallization fronts for a practically important case of the rate of crystal growth inversely proportional to the square root of time. Also, using the Laplace transformation method we have found an analytical solution for a plane crystallization front in the case of constant rate of crystal growth. The

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PII: S0017-9310(02)00349-6

Nomenclature

C	gas concentration
C_0	initial gas concentration in a melt
C_f	gas concentration in the crystallization front
C_{liq}	limiting solubility of a gas in a liquid phase
C_s	limiting solubility of a gas in a solid phase
$\widetilde{C}$	dimensionless gas concentration, $(C - C_0)/(C_0 - C_s)$
$\widetilde{C}_f$	dimensionless gas concentration in the crystallization front
$\widetilde{C}^*$	modified dimensionless gas concentration
D	coefficient of gas diffusion in a melt
K	proportionality factor in the dependence of the rate of crystallization front motion on time
t	time
V	velocity of crystallization front
V_0	constant velocity of crystallization front
X	coordinate of crystallization front
x	coordinate
$\hat{x}$	coordinate related to crystallization front
Greek symbols	
α	proportionality factor in the dependence of the diffusional layer thickness on time
γ	modified self-similar variable, $\eta/2\sqrt{D} + \kappa$
δ_d	diffusional layer thickness
η	self-similar variable, $\hat{x}/\sqrt{t}$
κ	coefficient, $K/\sqrt{D}$
τ	dimensionless time, $V_0^2 t/D$
χ	dimensionless coordinate, $V_0 t/D$
Subscripts	
f	refers to a crystallization front
liq	refers to a liquid phase
s	refers to a solid phase

plane front corresponds to successive crystallization, a spherical one to a growing single crystallization center originating in the process of heterogeneous or homogeneous nucleation.

2. Statement of the problem

We consider the problem of displacement of the gas dissolved in a melt by a plane and a spherical crystallization fronts. In both cases (plane and spherical symmetric) the x-axis coincided with the outer normal to the crystal surface. The boundary-value problem is written as follows:

The equation of diffusion

$$\frac{\partial C}{\partial t} = D\frac{1}{x^l}\frac{\partial}{\partial x}\left(x^l\frac{\partial C}{\partial x}\right). \tag{1}$$

The initial and boundary conditions

$$C = C_0 \quad \text{for } t = 0,$$

$$-D\frac{\partial C}{\partial x} = V(C - C_s) \quad \text{for } x = X, \tag{2}$$

$$C \to C_0 \quad \text{for } x \to \infty.$$

Here D is the coefficient of gas diffusion in a melt, $X = X(t)$ is the coordinate of the crystallization front, and $V = \mathrm{d}X/\mathrm{d}t$ is the rate of crystal growth. The values $l = 0$ and 2 correspond to the plane and the spherically symmetric cases.

We introduce the dimensionless concentration $\widetilde{C} = (C - C_0)/(C_0 - C_s)$ and transform to the coordinate system associated with the crystallization front ($\hat{x} = x - X$). In this case the boundary-value problem (1) and (2) is represented in the form

$$\frac{\partial\widetilde{C}}{\partial t} - V\frac{\partial\widetilde{C}}{\partial\hat{x}} = D\frac{1}{(\hat{x}+X)^l}\frac{\partial}{\partial\hat{x}}\left((\hat{x}+X)^l\frac{\partial\widetilde{C}}{\partial\hat{x}}\right), \tag{3}$$

$$\widetilde{C} = 0 \quad \text{for } t = 0, \tag{4}$$

$$-D\frac{\partial\widetilde{C}}{\partial\hat{x}} = V(\widetilde{C} + 1) \quad \text{for } \hat{x} = 0,$$

$$\widetilde{C} \to 0 \quad \text{for } \hat{x} \to \infty. \tag{5}$$

Problem (3)–(5) should be supplemented with the equation of the dependence of the speed of the front of phase transition on the time $V = V(t)$ which is taken from the solution of the melt crystallization problem. In the present work we consider two practically important cases of solidification. In the first case the melt crystallizes following the equilibrium mechanisms; this is the case when the overcooling of the melt at the crystallization front can be neglected (the Stefan problem); this approximation is adequate for the problems of solidification of large volumes. In the given case the rate of crystal growth is inversely proportional to the square root of time [6]. In the second case, solidification follows the nonequilibrium mechanism; this is the case when the overcooling of the melt at the crystallization front is equal to the overcooling of the melt far from the crystal; small volumes and thin specimens crystallize following this mechanism. In this case, the rate of crystal growth is constant [7]. It is assumed in both cases that the overcooling of the melt far from the solidification front is constant.

3. Analytical solutions and results

3.1. Solution in the case of equilibrium crystallization

When the rate of crystal growth is inversely proportional to the square root of time $V(t) = K\sqrt{t}$, problem (3)–(5) has a self-similar solution. We introduce the variable $\eta = \hat{x}/\sqrt{t}$. Then, the diffusion equation (3) is reduced to the ordinary differential equation

$$\widetilde{C}'' + f(\eta)\widetilde{C}' = 0, \tag{6}$$

where $f(\eta) = l/(\eta + 2K) + (\eta/2 + K)/D$. Boundary conditions (5) will have the form

$$-D\widetilde{C}' = K(\widetilde{C} + 1) \quad \text{for } \eta = 0,$$
$$\widetilde{C} \to 0 \quad \text{for } \eta \to \infty. \tag{7}$$

Integrating (6) subject to (7), we obtain

- for a plane case

$$\widetilde{C} = \frac{\sqrt{\pi}\kappa e^{\kappa^2}\operatorname{erfc}(\gamma)}{1 - \sqrt{\pi}\kappa e^{\kappa^2}\operatorname{erfc}(\kappa)}; \tag{8a}$$

- for the spherically symmetric case

$$\widetilde{C} = \frac{2\kappa^2[\kappa e^{\kappa^2-\gamma^2}/\gamma - \sqrt{\pi}\kappa e^{\kappa^2}\operatorname{erfc}(\gamma)]}{1 - 2\kappa^2[1 - \sqrt{\pi}\kappa e^{\kappa^2}\operatorname{erfc}(\kappa)]}. \tag{8b}$$

Here $\gamma = \eta/(2\sqrt{D}) + \kappa$; $\kappa = K/\sqrt{D}$. The graphs of the dependence $\widetilde{C}(\eta)$ for a plane and the spheric cases are shown in Fig. 1. Fig. 2 presents a comparison of the solution (8a) with the numerical solution obtained in [1] for the particular case of $\kappa = 1$.

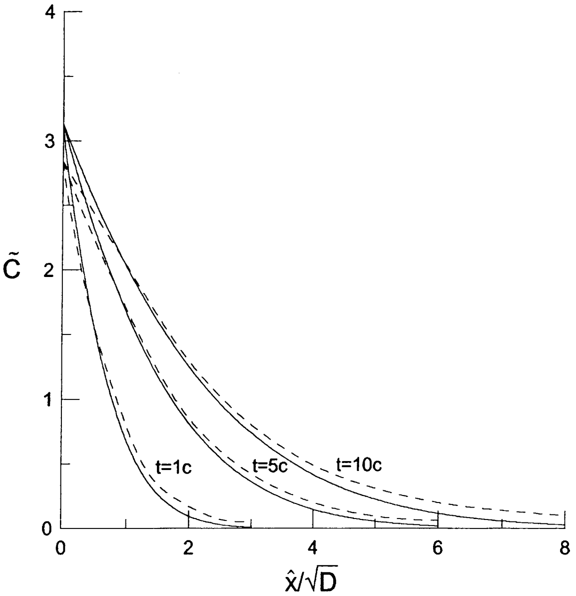

Fig. 2. Dependence of the gas concentration $\widetilde{C}$ on the $\hat{x}$ coordinate for the plane case for three different values of t in the case of the crystal growth rate inversely proportional to the square root of time, $\kappa = 1$. Solid lines show analytical solution (8a), the dashed lines represent the numerical calculation presented in [1].

It is seen from solutions (8a) and (8b) that at the crystallization front ($\eta = 0$) the concentration $\widetilde{C}_f$ is

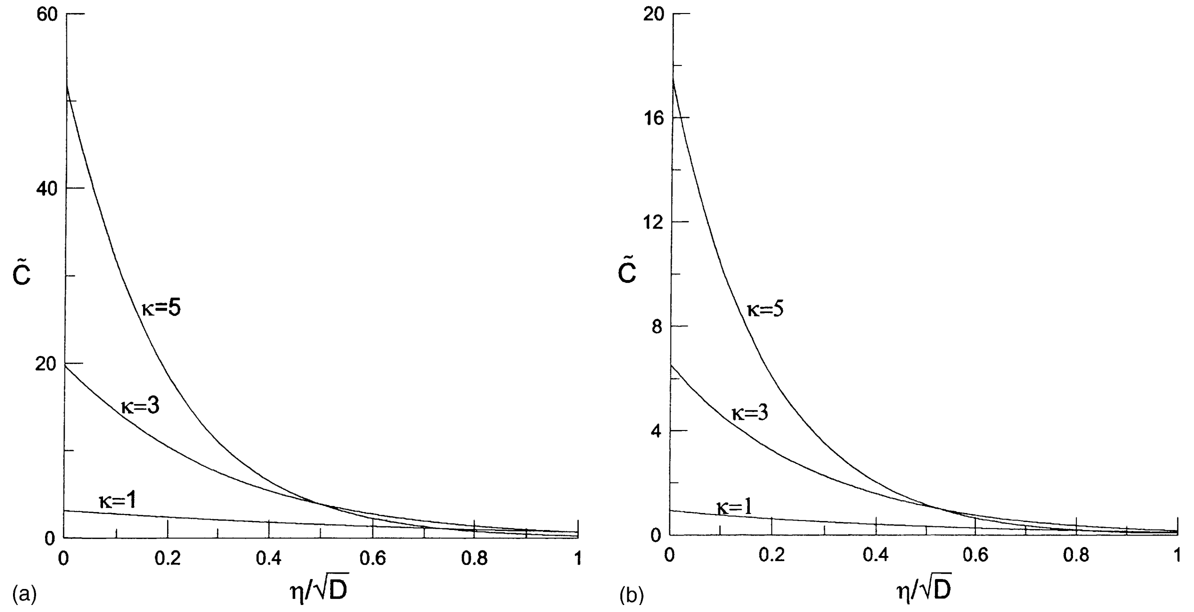

Fig. 1. Dependence of the gas concentration $\widetilde{C}$ on the self-similar variable η for three different values of the parameter κ in the case of the crystal growth rate inversely proportional to the square root of time: (a) for the plane case; (b) for the spherically symmetric case.

instantly established and remains constant during the whole process:

- for the plane case

$$\tilde{C}_{\mathrm{f}} = \frac{\sqrt{\pi}\kappa e^{\kappa^2}\operatorname{erfc}(\kappa)}{1-\sqrt{\pi}\kappa e^{\kappa^2}\operatorname{erfc}(\kappa)}; \tag{9a}$$

- for the spherically symmetric case

$$\tilde{C}_{\mathrm{f}} = \frac{2\kappa^2[1-\sqrt{\pi}\kappa e^{\kappa^2}\operatorname{erfc}(\kappa)]}{1-2\kappa^2[1-\sqrt{\pi}\kappa e^{\kappa^2}\operatorname{erfc}(\kappa)]}. \tag{9b}$$

It follows from solutions (8a) and (8b) that the diffusion layer thickness δ_{d} defined as $\tilde{C}(t,\delta_{\mathrm{d}})/\tilde{C}_{\mathrm{f}} = 1/e$ grows proportionally to the square root of time: $\delta_{\mathrm{d}} = \alpha\sqrt{Dt}$. The proportionality factor α is determined from the relations: $\operatorname{erfc}(\alpha/2+\kappa)/\operatorname{erfc}(\kappa) = 1/e$ for the plane case and $[\kappa e^{\kappa^2-(\alpha/2+\kappa)^2}/(\alpha/2+\kappa) - \sqrt{\pi}\kappa e^{\kappa^2}\operatorname{erfc}(\alpha/2+\kappa)]/[1-\sqrt{\pi}\kappa e^{\kappa^2}\operatorname{erfc}(\kappa)] = 1/e$—for the spherically symmetric case.

At large values of κ, using asymptotic representation of the additional integral of errors, in the vicinity of the crystallization front for the plane and spherically symmetric case we obtain

$$\tilde{C} \simeq \tilde{C}_{\mathrm{f}} e^{-\kappa\eta/\sqrt{D}}, \quad \tilde{C}_{\mathrm{f}} \simeq 2\kappa^2/(1+l), \quad \alpha \simeq 1/\kappa.$$

It is seen that with increase in the solidification rate determined by the parameter K, the gas concentration $\tilde{C}_{\mathrm{f}}$, instantly established in the crystallization front becomes higher and the coefficient α, which characterizes the diffusional layer thickness, decreases.

Since the concentration of the gas in the crystallization front remains constant during the whole process, then to exclude the formation of gas bubbles, it is necessary to satisfy the following conditions: the concentration of the gas in the crystallization front C_{f} must not exceed the limiting solvability of the gas in the liquid phase C_{liq}:

$$C_{\mathrm{f}} < C_{\mathrm{liq}} \quad \text{or} \quad (C_0 - C_{\mathrm{s}})\tilde{C}_{\mathrm{f}} + C_0 < C_{\mathrm{liq}}. \tag{10}$$

It is seen from relation (10) that there are three techniques for preventing gas evolution in the process of crystallization: (1) decrease in the initial concentration of a gas in a melt; (2) decrease of the rate of crystallization; (3) increase in the solubility of a gas in the liquid phase, for example, by increasing the pressure.

3.2. Solution in the case of nonequilibrium crystallization

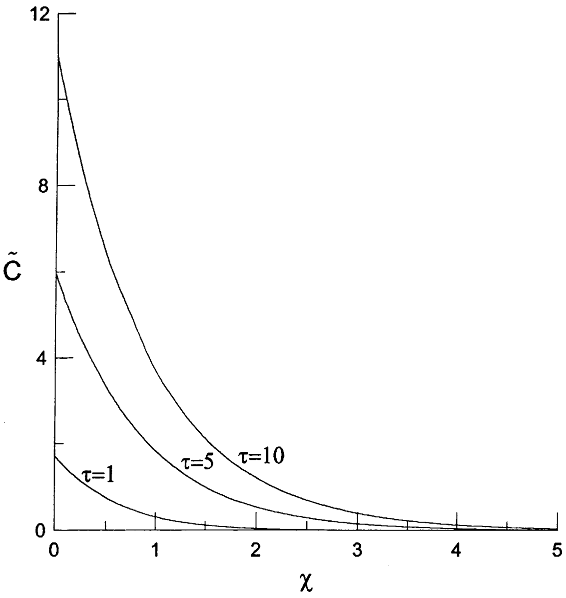

Fig. 3. Dependence of the gas concentration $\tilde{C}$ on the χ coordinate for three different values of τ in the case of a constant rate of crystal growth.

For a plane crystallization front ($l = 0$) moving with the constant velocity $V(t) = V_0$ the solution of problem (3)–(5) can also be obtained analytically. By performing the replacement $\tilde{C}^* = \tilde{C}e^{\tau/4+\chi/2}$ and thus excluding the convective term from the equation of diffusion (3), with the aid of the Laplace transformation, we obtain

$$\tilde{C} = \sqrt{\frac{\tau}{\pi}}e^{-\chi^2/4\tau-\chi/2-\tau/4} + \frac{1}{2}(1-\chi+\tau)e^{-\chi}\operatorname{erfc}\left(\frac{\chi}{2\sqrt{\tau}}-\frac{\sqrt{\tau}}{2}\right) - \frac{1}{2}\operatorname{erfc}\left(\frac{\chi}{2\sqrt{\tau}}+\frac{\sqrt{\tau}}{2}\right), \tag{11}$$

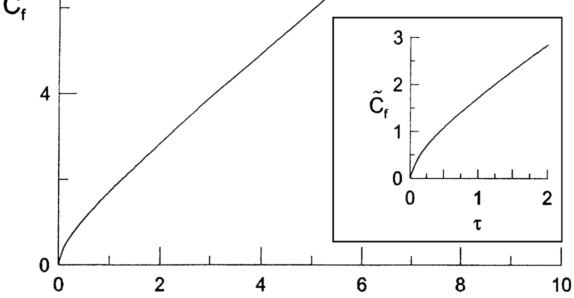

Fig. 4. Dependence of the gas concentration at the crystallization front $\tilde{C}_{\mathrm{f}}$ on the time τ in the case of constant rate of crystal growth; in the inset, the detailed representation of the vicinity of the zero.

where $\tau = V_0^2 t/D$ and $\chi = V_0\hat{x}/D$. Fig. 3 presents the graphs of the function $C(\chi)$ for three different times τ. Fig. 4 demonstrates the concentration of the gas in the crystallization front on time.

When $\tau \gg 1$, we obtain

$$\widetilde{C} \simeq 1 + \tau, \quad \delta_{\mathrm{d}} \simeq 1.$$

It is seen that in contrast to the equilibrium concentration, the nonequilibrium concentration of a gas at the phase change front increases with time and the thickness of the diffusional layer tends to a constant value. Therefore, in spite of the magnitude of the initial gas concentration, of course, if it exceeds the solubility of the gas in the solid phase, the concentration of the gas at the crystallization front will exceed, more or less rapidly, the critical one and gas evolution will begin.

It should be noted that expression (11) obtained differs from formula (20) given in [1]. However, the results calculated by formula (11) and presented in Figs. 3 and 4 virtually coincide with the data presented in Figs. 2 and 3 of [1]. From this it follows that it quite well may be that formula (20) in [1] has a misprint and it should look like formula (11) of the present paper.

We have failed to find an analytical solution of problem (3)–(5) for a spherical crystal growing with a constant rate.

4. Conclusions

We have considered the problem of the displacement of the gas dissolved in the melt by plane and spherical phase change fronts. When the crystal growth rate is inversely proportional to the square root of time, self-similar solutions have been found. It is shown that at the phase change front the concentration C_{f} is instantly established which remains constant during the entire process of crystallization. The criterion of the absence of gas evolution is given which owes its origin to segregation. For a plane crystallization front, in the case of a constant rate of crystal growth, an analytical solution has been found with the aid of the Laplace transformation. It is shown that at large times the concentration of the gas at the crystallization front increases linearly with time as a result of which gas evolution is virtually unavoidable.

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