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ANALYTICAL SOLUTION OF THE PROBLEM OF DISPLACEMENT OF A GAS DISSOLVED IN A MELT BY PLANE AND SPHERICAL CRYSTALLIZATION FRONTS

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Self-similar solutions of the problem of displacement of a gas dissolved in a melt by plane and spherical crystallization fronts are found for the case where the crystal growth rate is inversely related to the square root of time. A criterion of the absence of gas displacement due to segregation is found. The problem for a plane crystallization front moving with a constant velocity is analytically solved by means of the Laplace transform method.

Key words: *crystallization front, gas segregation melt, self-similar solution, diffusion layer.*

Introduction. As is known, crystallization is sometimes accompanied by gas displacement leading to formation of pores in the solid phase, which considerably affect the properties of the material obtained. This results from the fact that the gas solubility in the solid phase $C_{\rm s}$ is significantly lower than in the liquid phase $C_{\rm liq}$. If the initial concentration of the gas dissolved in the melt is $C_0 > C_{\rm s}$, the gas, which cannot be trapped by the solid phase during solidification, is displaced by the moving crystallization front. The problem of segregation of the gas dissolved in the melt by a plane phase-transition front is numerically solved in [1].

Gas-bubble nucleation begins at the moment when the gas concentration at the crystallization front exceeds a critical point. At low crystallization rates, gas bubbles are mainly formed at the growing crystal surface [2]; at high rates, gas displacement is possible within the whole volume of the substance. Further, the bubbles formed are trapped by the solid phase [3]. At low crystallization rates, the trapped bubble retains contact with the liquid phase and continues to be a drain for the displaced gas. Due to this, columnar gas inclusions are formed in the solid phase [4]. The average length of the trapped inclusions decreases with increasing crystallization rate, and their density increases. The form of trapped inclusions is close to spherical for crystallization rates higher than $3.5 \cdot 10^{-3}$ cm/sec. Note that the crystallization rates are orders higher than the value given in real regimes of solidification of metal melts, especially solidification of thin specimens.

Since the densities of most metals and alloys in the solid phase are higher than those in the liquid phase, a cavitation mechanism of formation of gas cavities is also possible during spontaneous crystallization. However, this problem requires careful analysis and is not considered here.

The case where the crystal growth rate is inversely proportional to the square root of time is important from the practical point of view. Self-similar solutions of the problem of displacement of the gas dissolved in the melt by plane and spherical crystallization fronts are found in the present paper. The problem is analytically solved by means of the Laplace transform method for a plane crystallization front and a constant growth rate of the crystal. The plane front corresponds to sequential crystallization, and the spherical front refers to a growing single crystallization nucleus resulting from heterogeneous or homogeneous nucleation.

Formulation of the Problem. Let us consider the problem of displacement of the gas dissolved in the melt by plane and spherical crystallization fronts. In both cases, the x axis coincides with the external normal to the crystal surface. The boundary-value problem is written as follows:

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— the diffusion equation

$$\frac{\partial C}{\partial t} = D\,\frac{1}{x^l}\,\frac{\partial}{\partial x}\Big(x^l\,\frac{\partial C}{\partial x}\Big); \tag{1}$$

— the initial and boundary conditions

$$\begin{gathered} C = C_0 \quad \text{for} \quad t = 0, \\ -D\,\frac{\partial C}{\partial x} = V(C - C_{\rm s}) \quad \text{for} \quad x = X, \qquad C \to C_0 \quad \text{for} \quad x \to \infty. \end{gathered} \tag{2}$$

Here D is the coefficient of gas diffusion in the melt, $X = X(t)$ is the coordinate of the crystallization front, and $V = dX/dt$ is the crystal growth rate; $l = 0$ and $l = 2$ correspond to the plane and spherical-symmetrical cases. The values of initial concentration and the maximum gas solubility in the solid and liquid phases are given in [5, 6].

Let us introduce a dimensionless concentration $\tilde{C} = (C - C_0)/(C_0 - C_{\rm s})$ and pass into a system of coordinates fitted to the crystallization front ($\hat{x} = x - X$). In this case, the boundary-value problem (1), (2) is written in the form

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

$$-D\,\frac{\partial \tilde{C}}{\partial \hat{x}} = V(\tilde{C} + 1) \quad \text{for} \quad \hat{x} = 0, \qquad \tilde{C} \to 0 \quad \text{for} \quad \hat{x} \to \infty; \tag{4}$$

$$\tilde{C} = 0 \quad \text{for} \quad t = 0. \tag{5}$$

Problem (3)–(5) shall be supplemented with an equation for the phase-transition front velocity versus time $V = V(t)$, which follows from the solution of the melt-crystallization problem. Two cases of solidification of practical importance are considered below. In the first case, the crystal growth rate is inversely related to the square root of time. Thus, large volumes of a substance are usually crystallized [7]. In the second case, the crystal growth rate is constant, which is typical, for example, for the initial stage of the phase transition [7].

Analytical Solutions and Analysis of Results. *The solution for the case of the crystal growth rate inversely proportional to the square root of time.* For $V(t) = K/\sqrt{t}$, problem (3)–(5) has a self-similar solution. Let us introduce a variable $\eta = \hat{x}/\sqrt{t}$. Then, the equation of diffusion (3) reduces to the ordinary differential equation

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

where $f(\eta) = l/(\eta + 2K) + (\eta/2 + K)/D$. The boundary conditions (4) are written in the form

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

Integrating (6) with allowance for (7), we obtain

$$\tilde{C} = \frac{\sqrt{\pi}\,æ\exp{(æ^2)}\,\mathrm{erfc}\,(\gamma)}{1 - \sqrt{\pi}\,æ\exp{(æ^2)}\,\mathrm{erfc}\,(æ)} \tag{8a}$$

for the plane case or

$$\tilde{C} = \frac{2æ^2[æ\exp{(æ^2 - \gamma^2)}/\gamma - \sqrt{\pi}\,æ\exp{(æ^2)}\,\mathrm{erfc}\,(\gamma)]}{1 - 2æ^2[1 - \sqrt{\pi}\,æ\exp{(æ^2)}\,\mathrm{erfc}\,(æ)]} \tag{8b}$$

for the spherical-symmetrical case. Here $\gamma = \eta/(2\sqrt{D}) + æ$ and $æ = K/\sqrt{D}$.

The dependences $\tilde{C}(\eta)$ for the plane and spherical-symmetrical cases are plotted in Fig. 1. Figure 2 shows the comparison of solution (8a) with the numerical solution obtained in [1] for the particular case $æ = 1$.

Solutions (8a) and (8b) show that the gas concentration $\tilde{C}_{\rm f}$ is instantaneously set at the crystallization front ($\eta = 0$) and remains constant during the whole process:

$$\tilde{C}_{\rm f} = \frac{\sqrt{\pi}\,æ\exp{(æ^2)}\,\mathrm{erfc}\,(æ)}{1 - \sqrt{\pi}\,æ\exp{(æ^2)}\,\mathrm{erfc}\,(æ)}$$

for the plane case or

$$\tilde{C}_{\rm f} = \frac{2æ^2[1 - \sqrt{\pi}\,æ\exp{(æ^2)}\,\mathrm{erfc}\,(æ)]}{1 - 2æ^2[1 - \sqrt{\pi}\,æ\exp{(æ^2)}\,\mathrm{erfc}\,(æ)]}$$

for the spherical-symmetrical case.

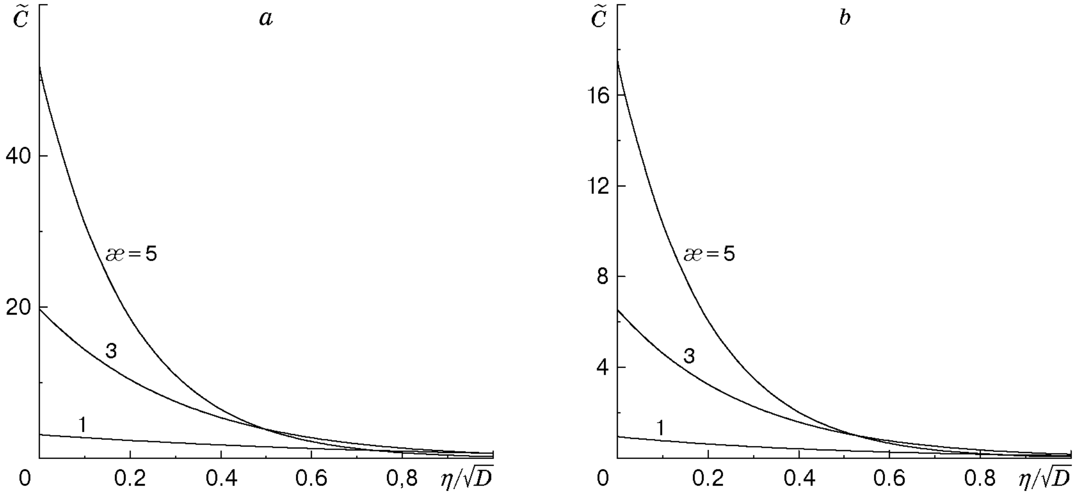

Fig. 1. Dependence of the gas concentration $\tilde{C}$ on the self-similar variable η for $V(t) = K/\sqrt{t}$ in the plane case (a) and in the spherical-symmetrical case (b).

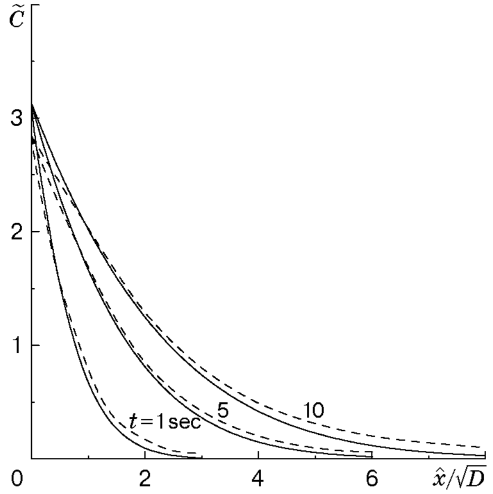

Fig. 2. Dependence of the gas concentration $\tilde{C}$ on the $\hat{x}$ coordinate for the plane case for $V(t) = K/\sqrt{t}$ and $æ = 1$: the solid curves show the analytical solution (8a) and the dashed curves refer to the numerical calculation [1].

From solutions (8a) and (8b), it also follows that the diffusion-layer thickness $\delta_{\rm dif}$ determined by the relation $\tilde{C}(t, \delta_{\rm dif})/\tilde{C}_{\rm f} = 1/e$ increases in proportion to the square root of time: $\delta_{\rm dif} = \alpha\sqrt{Dt}$. The proportionality coefficient α is determined from the expressions $\operatorname{erfc}(\alpha/2 + æ)/\operatorname{erfc}(æ) = 1/e$ for the plane case and $[æ \exp(æ^2 - (\alpha/2 + æ)^2)/(\alpha/2 + æ) - \sqrt{\pi}\, æ \exp(æ^2) \operatorname{erfc}(\alpha/2 + æ)]/[1 - \sqrt{\pi} æ \exp(æ^2) \operatorname{erfc}(æ)] = 1/e$ for the spherical-symmetrical case.

The asymptotic representation of an additional error integral is used for large æ. In the vicinity of the crystallization front for the plane and spherical-symmetrical cases, we obtain

$$\tilde{C} \simeq \tilde{C}_{\rm f} \exp(-K\eta/D), \quad \tilde{C}_{\rm f} \simeq 2K^2/[(1 + l)D], \quad \alpha \simeq \sqrt{D}/K.$$

Obviously, with increasing solidification rate determined by the parameter K, the gas concentration $\tilde{C}_{\rm f}$ instantaneously established at the crystallization front also increases, and the constant α characterizing the diffusion-layer thickness decreases.

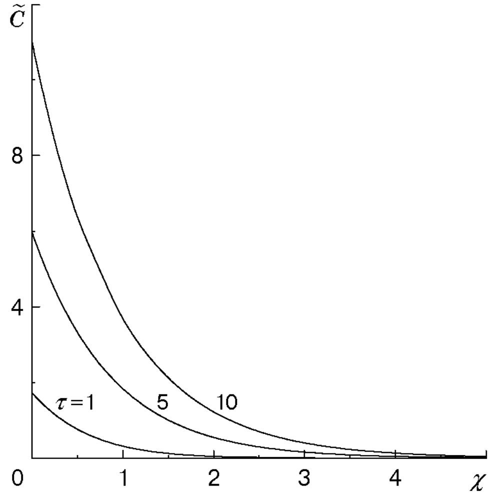

Fig. 3

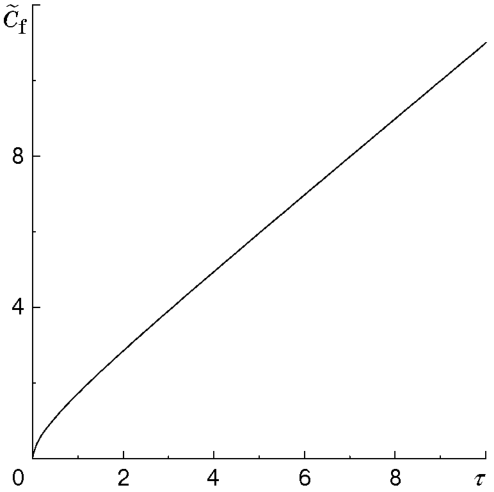

Fig. 4

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

Fig. 4. Dependence of the gas concentration at the crystallization front $\tilde{C}_{\rm f}$ on time τ in the case of a constant crystal growth rate.

Since the gas concentration at the crystallization front remains constant during the whole process, the following condition should be satisfied to avoid gas-bubble nucleation. The gas concentration at the crystallization front $C_{\rm f}$ should not exceed the limiting solubility of the gas in the liquid phase $C_{\rm liq}$:

$$C_{\rm f} < C_{\rm liq} \qquad \text{or} \qquad (C_0 - C_{\rm s})\tilde{C}_{\rm f} + C_0 < C_{\rm liq}. \tag{9}$$

It follows from relationship (9) that there are three ways to prevent gas displacement during the crystallization process: 1) decrease in the initial gas concentration in the melt, 2) decrease in the crystallization rate, and 3) increase in gas solubility in the liquid phase, for example, at the expense of a pressure increase.

Solution in the Case of a Constant Crystal Growth Rate. For the plane crystallization front ($l = 0$) moving with a constant velocity $V(t) = V_0$, the solution of problem (3)–(5) can also be found analytically. Note that such a solution was obtained in [1], but it does not correspond to the data of Figs. 2 and 3 presented in [1], i.e., a misprint seems to be introduced in formula (20) of [1]. Following [1], we again obtain the solution of problem (3)–(5). Substituting $\tilde{C}^* = \tilde{C}\exp(\tau/4 + \chi/2)$ and, thus, eliminating the convective term from the diffusion equation (3), we use the Laplace transform method to obtain

$$\tilde{C} = \sqrt{\frac{\tau}{\pi}}\,\exp\Big(-\frac{\chi^2}{4\tau} - \frac{\chi}{2} - \frac{\tau}{4}\Big) + \frac{1}{2}(1 - \chi + \tau)\exp(-\chi)\,\mathrm{erfc}\Big(\frac{\chi}{2\sqrt{\tau}} - \frac{\sqrt{\tau}}{2}\Big) - \frac{1}{2}\,\mathrm{erfc}\Big(\frac{\chi}{2\sqrt{\tau}} + \frac{\sqrt{\tau}}{2}\Big), \tag{10}$$

where $\tau = V_0^2 t/D$ and $\chi = V_0\hat{x}/D$.

Figure 3 shows the dependence $\tilde{C}(\chi)$ for different values of τ. Figure 4 shows the gas concentration at the crystallization front versus time. For $\tau \gg 1$, we have $\tilde{C} \simeq 1 + \tau$ and $\delta_{\rm dif} \simeq 1$. It follows from Fig. 4 that the gas concentration at the phase-transition front increases in time in the case of a constant crystal growth rate, in contrast to the case $V(t) = K/\sqrt{t}$, and the diffusion-layer thickness tends to a constant value. Therefore, for all initial gas concentrations exceeding gas solubility in the solid phase, the gas concentration at the crystallization front exceeds its critical point at a certain moment, and gas displacement begins.

The results calculated by formula (10) and presented in Figs. 3 and 4 coincide with the data shown in Figs. 2 and 3 of [1]. Thus, formula (20) of [1] should be replaced by formula (10) of the present paper.

Problem (3)–(5) for a spherical crystal with a constant growth rate could not be analytically solved.

Conclusions. The problem of displacement of a gas dissolved in a melt by plane and spherical phase-transition fronts is considered. Self-similar solutions are found for the case where the crystal growth rate is inversely proportional to the square root of time. It is shown that a certain gas concentration is instantaneously established at the phase-transition front and remains constant during the whole crystallization process. A criterion of the absence of gas displacement caused by segregation is obtained. For a plane crystallization front, in the case of a constant crystal growth rate, an analytical solution is found by means of the Laplace transform method. It is shown that, at large times, the gas concentration at the crystallization front increases linearly with time, which makes gas displacement almost inevitable.

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REFERENCES

1. M. A. Bianchi and R. Viskanta, "Gas segregation during solidification process," *Int. J. Heat Mass Transfer*, **40**, No. 9, 2035–2043 (1997).
2. W. R. Wilcox and V. H. S. Kuo, "Gas bubble nucleation during crystallization," *J. Crystal Growth*, **19**, 221–228 (1973).
3. Ya. E. Geguzin and A. S. Dzyuba, "Gas release, nucleation and trapping of gas bubbles from the melt at the crystallization front," *Kristallografiya*, **22**, Issue 2, 348–353 (1977).
4. P. S. Wei, Y. K. Kuo, S. H. Chiu, and C. Y. Ho, "Shape of a pore trapped in solid during solidification," *Int. J. Heat Mass Transfer*, **43**, No. 2, 263–280 (2000).
5. G. M. Grigorenko and Yu. M. Pomarin, *Hydrogen and Nitrogen in Metals in Plasma Melting* [in Russian], Naukova Dumka, Kiev (1989).
6. Yu. A. Kunitsky, V. N. Korzhik, and Yu. S. Borisov, *Noncrystalline Metal Materials and Coatings in Technology* [in Russian], Tekhnika, Kiev (1988).
7. B. Ya. Lubov, *Theory of Crystallization in Large Volumes* [in Russian], Nauka, Moscow (1975).