HEAT AND MASS TRANSFER DURING GROWTH OF A SPHERICAL PARTICLE FROM THE LIQUID PHASE

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Heat and mass transfer during growth of a spherical particle from the liquid phase is analyzed on the example of the crystallization process. The results of numerical simulation are confirmed by experimental data.

Despite the substantial achievements made in separating and purifying substances by crystallization methods, the kinetic aspect of this process remains still very little explored. This study will deal with the dependence of the crystal growth rate on the dimensions of the crystal and on the physical properties of the system. The problem is formulated on the assumption that the crystal has the shape of a sphere and that the change in the velocity of its movement due to the growth is so small that the process of heat and mass transfer can at every instant of time be regarded as steady [1].

Fundamental Equations and Boundary Conditions. The original system of equations of convective heat and mass transfer, written in a spherical system of coordinates tied to the center of the particle and transformed so as to take into account the steadiness of the symmetry of flow, is

equation of flow continuity

$$\frac{\partial}{\partial r}(r^2 w_r \sin\theta) + \frac{\partial}{\partial\theta}(r w_\theta \sin\theta) = 0; \tag{1}$$

Navier–Stokes equations

$$w_r - \frac{\partial w_r}{\partial r} + \frac{w_\theta}{r}\frac{\partial w_r}{\partial\theta} - \frac{w_\theta^2}{r} = -\frac{1}{\rho}\frac{\partial P}{\partial r} + \nu\left(\nabla^2 w_r - \frac{2}{r^2}w_r - \frac{2}{r^2}\frac{\partial w_\theta}{\partial\theta} - \frac{2}{r^2}w_\theta \operatorname{ctg}\theta - \frac{2}{r^2\sin\theta}\right), \tag{2}$$

$$w_r\frac{\partial w_\theta}{\partial r} + \frac{w_\theta}{r}\frac{\partial w_\theta}{\partial\theta} + \frac{w_r w_\theta}{r} = -\frac{1}{\rho}\frac{1}{r}\frac{\partial P}{\partial\theta} + \nu\left(\nabla^2 w_\theta + \frac{2}{r^2}\frac{\partial w_r}{\partial\theta} - \frac{w_\theta}{r^2\sin^2\theta}\right); \tag{3}$$

equation of convective heat transfer

$$w_r\frac{\partial T}{\partial r} + \frac{w_\theta}{r}\frac{\partial T}{\partial\theta} = a\nabla^2 T; \tag{4}$$

and equation of convective mass transfer

$$w_r\frac{\partial C}{\partial r} + \frac{w_\theta}{r}\frac{\partial C}{\partial\theta} = D\nabla^2 C, \tag{5}$$

with the Laplace operator ∇^2

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\frac{\partial}{\partial\theta}\right). \tag{6}$$

The system of equations (1)-(6) is solved for the boundary conditions

at the surface of the particle ($r = R_0$)

$$w_r = w_\theta = 0, \tag{7}$$

$$g w(l) = -\lambda\frac{\partial T}{\partial r}\bigg|_{r=R_0},\quad w(l) = -D\frac{\partial C}{\partial r}\bigg|_{r=R_0}; \tag{8}$$

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far from the particle ($r \to \infty$)

$$w_r = w_0 \cos\theta,\ w_\theta = w_0 \sin\theta,\ T = T_0,\ C = C_0; \tag{9}$$

and at the axis of symmetry (θ = 0° and θ = 180°)

$$\left.\frac{\partial w_r}{\partial\theta}\right|_{\theta=0^\circ,180^\circ} = 0,\ w_\theta = 0,$$

$$\left.\frac{\partial C}{\partial\theta}\right|_{\theta=0^\circ,180^\circ} = 0,\ \left.\frac{\partial T}{\partial\theta}\right|_{\theta=0^\circ,180^\circ} = 0. \tag{10}$$

The linear growth rate $w(l)$ in the boundary conditions is determined by the intensity at which material deposits on the surface of the growing particle. Under conditions of crystallization this rate $w(l)$ depends on the maximum oversaturation at the crystal surface [2-4]:

$$w(l) = k_0\left[(C - C^*)\Big|_{\substack{r=R_0\\ \theta=0}}\right]^{n_0}. \tag{11}$$

The system of equations (1)-(11) becomes a closed one when supplemented with an equation relating the equilibrium concentration C^* to the temperature T:

$$C^* = A + BT. \tag{12}$$

<u>Numerical Solution.</u> The original system of equations (1)-(6) will be put in the "flow function–vortex–temperature–concentration" form convenient for numerical integration. According to the procedure in [5], this system will be written as

$$R^2\left[\frac{\partial}{\partial r}\left(\frac{\omega}{R}\frac{\partial\Psi}{\partial\theta}\right) - \frac{\partial}{\partial\theta}\left(\frac{\omega}{R}\frac{\partial\Psi}{\partial r}\right)\right] = \nu\left\{\frac{\partial}{\partial r}\left[rR^3\frac{\partial}{\partial r}\left(\frac{\omega}{R}\right)\right] + \frac{\partial}{\partial\theta}\left[\frac{R^3}{r}\frac{\partial}{\partial\theta}\left(\frac{\omega}{R}\right)\right]\right\}; \tag{13}$$

$$\omega = -\frac{1}{R}\left\{\frac{\partial^2\Psi}{\partial r^2} + \frac{\sin\theta}{r^2}\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial\Psi}{\partial\theta}\right)\right\}; \tag{14}$$

$$\frac{\partial}{\partial r}\left[C\frac{\partial\Psi}{\partial\theta}\right] - \frac{\partial}{\partial\theta}\left[C\frac{\partial\Psi}{\partial r}\right] = D\left[\sin\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right) + \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial C}{\partial\theta}\right)\right]; \tag{15}$$

$$\frac{\partial}{\partial r}\left[T\frac{\partial\Psi}{\partial\theta}\right] - \frac{\partial}{\partial\theta}\left[T\frac{\partial\Psi}{\partial r}\right] = a\left[\sin\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right) + \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T}{\partial\theta}\right)\right], \tag{16}$$

with $R = r\sin\theta$. The boundary conditions here will be

at the surface of the particle ($r = R_0$)

$$\Psi = 0,\ \omega = -\frac{\partial}{\partial n}\left(\frac{1}{r}\frac{\partial\Psi}{\partial n}\right),$$

$$gw(l) = -\lambda\left.\frac{\partial T}{\partial r}\right|_{r=R_0},\ w(l) = -D\left.\frac{\partial C}{\partial r}\right|_{r=R_0}, \tag{17}$$

$$w(l) = k_0\left[(C - C^*)\Big|_{\substack{r=R_0\\ \theta=0}}\right]^{n_0},$$

$$C^* = A + BT;$$

far from the particle ($r \to \infty$)

$$\Psi = \frac{1}{2}r^2 w_0 \sin^2\theta,\ \omega = 0,\ T = T_0,\ C = C_0; \tag{18}$$

and at the axis of symmetry (θ = 0° and θ = 180°)

$$\Psi = 0,\ \omega = 0,$$

$$\left.\frac{\partial C}{\partial\theta}\right|_{\theta=0^\circ} = 0,\ \left.\frac{\partial T}{\partial\theta}\right|_{\theta=0^\circ} = 0. \tag{19}$$

The change from Eqs. (13)-(19) to difference equations has been thoroughly described elsewhere [6]. The grid radius and the method of grid construction were here selected pre-

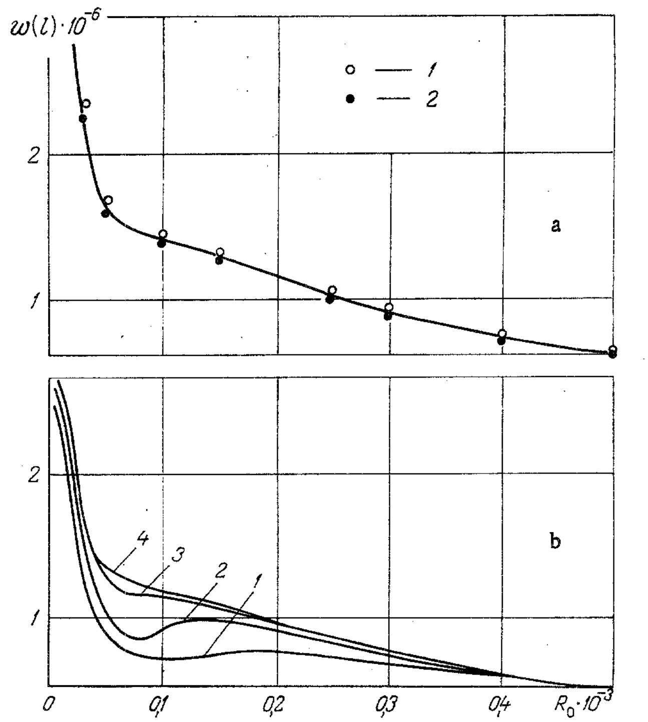

Fig. 1. Dependence of the growth rate $w(l)$ of a spherical particle on the dimension R_0, with $k_0 = 5.6\cdot 10^{-5}$ m/sec and $N_{Pr} = 12.5$, for (a) $N_{Sc} = 625$: $g = 100$ kJ/kg, 1) $g = 10$ kJ/kg; 2) $g = 1000$ kJ/kg; (b) $g = 10$ kJ/kg and 1) $N_{Sc} = 50$; 2) $N_{Sc} = 400$; 3) $N_{Sc} = 625$; 4) $N_{Sc} = 1000$ ($w(l)\cdot 10^{-6}$ m/sec and $R_0\cdot 10^{-3}$ m).

liminarily so as to shorten the computation time without loss of precision. Grids with radii $0 \leqslant r \leqslant 3R_0$ were considered and constructed as follows: number of radial nodes × number of angular nodes = 8 × 10, 10 × 12, 14 × 15, 14 × 20, 20 × 20, and 20 × 25. The 14 × 15 grid was ultimately selected. This choice had been based on the fact that further increases in the number of nodes hardly affected the precision while unjustifiably lengthening the computation time.

As the model system served a molten mixture of two substances with the following physical properties: $\rho_S = 1200$ kg/m^3, $\rho = 1163$ kg/m^3, $D = 0.9\cdot 10^{-9}$ m/sec, $\lambda = 1.01\cdot 10^{-6}$ W/m·°C, $\nu = 1.25\cdot 10^{-6}$ m^2/sec, $c_p = 1.55$ kJ/kg·°C, $g = 100$ kJ/kg, $A = 0.31$, and $B = 0.0125$ 1/°C. This system was selected as the model, because all effects associated the dependence of the growth rate on the particle size are most distinctly manifested in a melt. The kinetic constants in the equation for the growth rate had been determined earlier [7] on the basis of theoretical and experimental analysis of one-dimensional crystallization of a melt on a solid surface cooled without convection ($k_0 = 1.2\cdot 10^{-6}$ m/sec·K or $k_0 = 0.112\cdot 10^{-3}$ m/sec, $n_0 = 1$).

Results of Computations. Numerical simulation was done for a freely precipitating spherical particle as well as for a spherical particle moving in a stream with large-scale turbulent fluctuations ($L \gg R_0$). In the first case the velocity of the particle relative to the liquid phase was calculated according to the relation

$$w_0 = \sqrt{\frac{4}{3}\,\frac{(\rho_S - \rho)2R_0}{\rho\zeta}}, \tag{20}$$

with ζ denoting the drag coefficient for the particle in the liquid

$$\zeta = \begin{cases} 24/\mathrm{Re}, & \mathrm{Re} < 2, \\ 18.5/\mathrm{Re}^{0.6}, & \mathrm{Re} \geqslant 2. \end{cases}$$

Published data on the dependence of the growth rate of a single crystal on the heat of crystallization g are quite contradictory. According to calculations by these authors (Fig. 1a), a change of g within the 10-1000 kJ/kg range does not appreciably affect the crystal growth rate. Heat transfer could, therefore, be eliminated from further analysis and the original problem thus simplified.

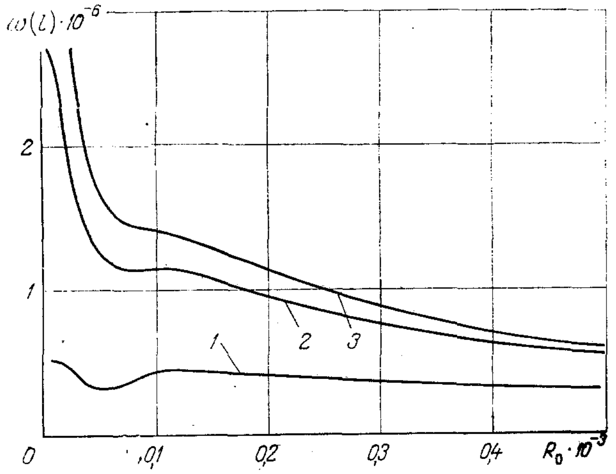

Fig. 2

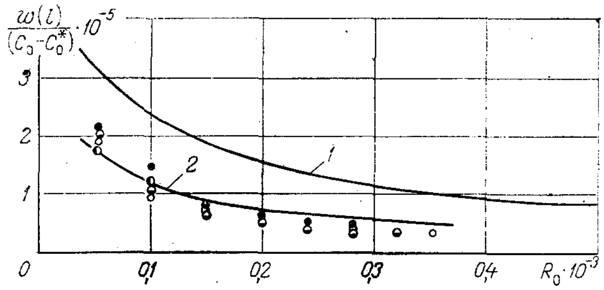

Fig. 3

Fig. 2. Dependence of the growth rate of a spherical particle w(*l*) on the dimension R_0, with $N_{Pr} = 12.5$, $N_{Sc} = 625$, and $g = 10$ kJ/kg, for: 1) $k_0 = 1.12\cdot10^{-5}$ m/sec; 2) $k_0 = 5.6\cdot10^{-5}$ m/sec; 3) $k_0 = 1.12\cdot10^{-4}$ m/sec.

Fig. 3. Dependence of the reference growth rate of a spherical particle $w(l)/(C - C^*)$ on the dimension R_0 during large-scale turbulent fluctuations ($\varepsilon_k = 2\cdot10^{-5}$ m^2/sec^3 and $\varphi = 10$ kg/m^3): 1) calculations for spherical particles; 2) calculations taking into account the lamellar shape of a particle; dots represent data in [11].

Unlike in expression (11) where determining the oversaturation at the surface $(C - C^*)|_{r=R_0,\ \theta=0°}$ is difficult, in engineering calculations the crystal growth rate is determined from the oversaturation of the original system and most often according to the approximate relation [9]

$$w(l) = k(T)\, R_0^m (C_0 - C_0^*)^{n_1}. \tag{21}$$

It is assumed, moreover, that the exponent m varies from −1 to 2 and that only the coefficient k(T) depends on the tempeature at which crystal growth occurs. According to the graph in Fig. 1b, however, the entire trend of the $w(l) = f(R_0)$ relation changes with changes in the value of the Schmidt number ($N_{Sc} = \nu/D$), i.e., with changing temperature of the crystallizable system.

Transition from purely diffusional growth to a growth process limited by surface kinetics is seen in Fig. 2 (curves 3 and 1, respectively). The "dip" of curve 1 is most likely associated with the effect of the diffusion flow on the growth rate of small particles, this diffusion flow ceasing to limit the growth of particles with a large radius R_0.

In most industrial crystallizers the crystal growth is accompanied by large-scale turbulent fluctuations in the liquid phase. These turbulent fluctuations are a consequence of the dissipation of energy which has been added to the system during stirring. When stirring is done by injection of an inert phase (gas or liquid), then the relative velocity of a moving particle can be determined according to the relation [10]

$$w_0 = 2.05\cdot10^{-3}\left(\frac{\rho_s}{\rho_s - \frac{1}{2}\rho}\right)^{\frac{1}{2}}\left(2R_0\rho_s\frac{\varepsilon_k}{\varphi^2}\right)^{\frac{1}{3}}. \tag{22}$$

The trend of the $w(l) = f(R_0)$ relation shown in Fig. 3 agrees with calculations based on expression (21), and the growth of particles is here limited by diffusion.

Theoretical and experimental data were compared (Fig. 3) taking into account the lamellar shape of particles of the crystallizing system. In the case of growth by the diffusion mechanism, the shape of a particle can be accounted for by the correction function f shown in [12]. If one assumes that lamellar crystals with face dimensions in the ratio 1:6:10 are equivalent to cylindrical particles with a radius-to-height ratio $R_c/h = 4$, then the value of this correction function will be 0.52.

In the case of large-scale turbulent fluctuations, therefore, the relation w(*l*) can be approximated with the expression (21). In the case of free precipitation, on the other hand, the dependence of $w(l)$ on the particle radius is more intricate and largely determined by the relation between diffusion and kinetic components of the process.

NOTATION

r, z, θ, spherical coordinates; R_0, radius of a spherical particle; n, distance from the surface of the sphere along the normal; w_r, radial component of the velocity of the liquid; w_θ, tangential component of the velocity of the liquid; w_0, velocity of the particle relative to the liquid; P, pressure; ρ, density of the liquid; ν, kinematic viscosity; D, diffusion coefficient; a, thermal diffusivity; T, temperature; C, concentration; C^*, equilibrium concentation; T_0, initial temperature; C_0, initial concentration; k_0, n_0, kinetic constants in the growth rate; A, B, constants in the temperature dependence of the equilibrium concentration; $w(l)$, linear growth rate; ψ, flow function; ω, vorticity; g, heat of crystallization; L, scale of turbulent fluctuations; ζ, drag coefficient for a particle in the liquid; $k(T)$, m, and n_1, constants in the equation for the growth rate; ρ_s, density of the solid phase; ρ_g, gas density; φ, solid content; ε_k, specific kinetic energy of the three-phase system; $N_{Re} = R_0 W_0/\nu$, Reynolds number; $N_{Sc} = \nu/D$, Schmidt number; and $N_{Pr} = \nu/a$, Prandtl number.

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MECHANISM OF MASS TRANSFER AFFECTING LIQUID METALS IN SINTERED COMPOSITE MATERIALS

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It is demonstrated that mass transfer of the liquid phase in sintered composite materials can occur as a result of restructurization of the refractory skeleton.

According to established concepts, mass transfer during interaction of sintered composites with liquid metals occurs by the diffusion mechanism and in porous bodies due to action of capillary forces [1, 2].

In this report attention will be drawn to the existence of still another mode of mass transfer in sintered composites, namely mass transfer caused by restructurization of the refractory skeleton.

In the experimental study conditions eliminating the possibility of mass transfer by diffusion and capillary forces were created. Compact spherical specimens, 20 mm in diameter,

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