DETERMINATION OF THE CONSTANTS OF MASS TRANSFER AND SURFACE REACTION FROM THE SOLUTION OF THE DIFFUSION PROBLEM WITH NONLINEAR BOUNDARY CONDITION FOR THE SATURATION AND DEGASSING OF LIQUID METAL

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The article suggests a model of mass transfer and a method of calculating the constants of mass transfer and of surface reaction from the results of measurements of the speed of saturation and degassing of an agitated liquid.

Processes of interaction of gases with a liquid are widely used in industry. However, many problems of the theory of mass exchange in systems of gas–liquid have not been treated with sufficient thoroughness, e.g., mass transfer in a liquid near the free surface and the regularities of the adsorption–desorption reactions on the phase boundary. This applies particularly to molten metals.

Saturation or degassing of a liquid metal within the framework of the phenomenological theory can be represented in the form of three successive stages: transfer in the gaseous and liquid phases and chemical reactions on the phase boundary, regarded as a single surface reaction. It is usually assumed that one of the stages (mass transfer in the liquid phase) is the slowest one, and thanks to that the analytical description of the entire process becomes simplified. However, it was pointed out, e.g., in [1], that this assumption is often not fulfilled, in cases of practical importance the speeds of mass transfer in the liquid and of the surface reaction are commensurable. Most often mass transfer in the gaseous phase proceeds much more rapidly.

The present article deals with the model of mass transfer in agitated liquid metal, with the reaction on the surface taken into account. The model is based on the assumption that in the metal near the free surface there exists a diffusion boundary layer. For molten metals and other liquids with high surface tension this assumption is quite substantiated because there is only a small probability that turbulent eddies penetrate as far as the metal–gas interface [2, p. 183]. By thickness of the boundary layer we mean the time-averaged and surface-averaged statistical dimension of the region adjacent to the gas–metal phase boundary where mass transfer is effected predominantly by molecular diffusion. We also assume that transfer in the gaseous phase does not affect the speed of the entire process. Regardless of the relatively small size of the diffusion boundary layer in liquid metal, the time during which an undistorted contact surface of the phases exists, which depends on the acutal hydrodynamic conditions, may also be fairly short. It is therefore advisable for greater generality of the statement of the problem to assume that the diffusion process in the boundary layer is nonsteady. Such an approach is not in contradiction to the theory of diffusion boundary layers because the usually adopted linear distribution of concentrations in it is also approximate [3, p. 154].

The mathematical statement of the problem is as follows: diffusion occurs through a plane-parallel layer of thickness a into agitated liquid metal with finite volume V in the case of saturation, or from liquid metal in the case of degassing. We write the equation of diffusion

$$D\,\frac{\partial^2 c}{dx^2}-\frac{\partial c}{\partial t}=0. \tag{1}$$

When dealing with a biatomic gas, we take it in the general case that the speed of the surface reaction is commensurable with the speed of diffusion. Then on the phase boundary x = 0 the boundary conditions for saturation and degassing are the following [4, p. 171]:

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TABLE 1. Experimental Data

No.	Temp., ℃	Gaseous phase	[S], %	[C], %
1	1640	$N_2+1\%\ H_2$	0,0092	0,120
2	1644	$N_2+1\%\ H_2$	0,0046	0,007
3	1620	N_2	0,0014	0,007
4	1630	vacuum	0,0070	0,006
5	1625	$Ar+1\%\ H_2$	0,0014	0,007
6	1620	$Ar+1\%\ H_2$	0,0150	0,050
7	1630	$N_2+1\%\ H_2$	0,0080	0,120
8	1635	$N_2+1\%\ H_2$	0,0080	0,120
9	1625	$N_2+1\%\ H_2$	0,0014	0,007

$$D\left.\frac{\partial c}{\partial x}\right|_{x=0} = K\left(c|_{x=0}^2 - c_e^2\right),\ t>0; \tag{2}$$

$$D\left.\frac{\partial c}{\partial x}\right|_{x=0} = Kc|_{x=0}^2,\ t>0. \tag{3}$$

The boundary condition on the inner boundary of the layer with thickness a is due to processes of agitation. We write Fick's first law for the mass of gas passing over the surface $x = a$:

$$dM = -D\frac{\partial c}{\partial x}Sdt. \tag{4}$$

We assume that the mixing is so intense that the gas diffusing through the boundary layer becomes uniformly distributed throughout the bulk of the melt within a negligibly short time, i.e., that the concentration $c|_{x=a}$ on the inner boundary of the layer is equal to the concentration in the bulk of the melt. Substituting $dM/dt = \partial c/\partial t|_{x=a}V$ in (4), we obtain the boundary condition on the inner face of the boundary layer

$$\left.\frac{\partial c}{dt}\right|_{x=a} = -D\frac{S}{V}\left.\frac{\partial c}{\partial x}\right|_{x=a} \tag{5}$$

We will regard the initial condition in the form

$$c|_{t=0} = c_0,\ x\geqslant 0. \tag{6}$$

Conditions (5) and (6) are the same for saturation and degassing. We introduce the dimensionless variables:

$$u = \frac{c}{c_0};\ \xi = \frac{Kc_e}{D}x;\ \Theta = \frac{K^2c_e^2}{D}t,$$

then Eqs. (1)-(3), (5), (6) assume the form

$$\frac{\partial^2 u}{\partial\xi^2} - \frac{\partial u}{\partial\Theta} = 0,\ 0\leqslant\xi\leqslant\alpha,\ \Theta>0; \tag{7}$$

$$u|_{\Theta=0} = u_0,\ \xi\geqslant 0; \tag{8}$$

$$\left.\frac{\partial u}{\partial\xi}\right|_{\xi=0} = u|_{\xi=0}^2 - 1,\ \Theta>0\ \text{(saturation)}; \tag{9}$$

$$\left.\frac{\partial u}{\partial\xi}\right|_{\xi=0} = u|_{\xi=0}^2,\ \Theta>0\ \text{(degassing)}; \tag{10}$$

$$\left.\frac{\partial u}{\partial\xi}\right|_{\xi=\alpha} = -\gamma\left.\frac{\partial u}{\partial\Theta}\right|_{\xi=\alpha},\ \Theta>0; \tag{11}$$

where

$$\alpha = \frac{Kc_e}{D}a;\ \gamma = \frac{Kc_eV}{DS};\ u_0 = \frac{c_0}{c}.$$

Problems (7)-(11) were solved numerically by the grid method according to the implicit schema [5]. In the semistrip $\Theta \geq 0$, $0 \leq \xi \leq \alpha$ the following square mesh grid was introduced: $\xi_i = ih$ $(i = 0, 1, 2, \ldots, n)$, $\Theta_j = j\tau$ $(j = 0, 1, 2, \ldots)$, where $h = \alpha/n$ is the step along the ξ

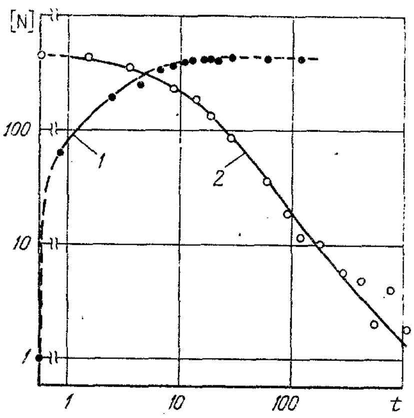

Fig. 1. Change of the nitrogen concentration in dissolution (curve 1) and desorption (curve 2) vs time: 1) data No. 1, weight 2.8 g, [O] = 0.0016%; 2) data No. 6, weight 2.6 g, [O] = 0.0032% (see Table 1). t, sec; [N], wt.%·10^4.

axis; τ is the step along the Θ axis. We denote $u_i^j = u(\xi_i, \Theta_j)$ and replace the partial derivatives in Eq. (6) be finite differences, using the values of the concentration in the nodes of the grid:

$$\frac{\partial u}{\partial\Theta} \approx \frac{1}{\tau}(u_i^{j+1} - u_i^j), \quad \frac{\partial^2 u}{\partial\xi^2} \approx \frac{1}{2h^2}(u_i^{j+1} - 2u_{i-1}^{j+1} + u_{i-1}^{j+1} + u_{i+1}^j - 2u_i^j + u_{i-1}^j). \tag{12}$$

We express the boundary conditions (9) and (10) through the concentration in the nodes i = 0 and i = 1 of the layer with the number j:

$$\frac{u_1^j - u_0^j}{h} = (u_0^j)^2 - 1, \quad \frac{u_1^j - u_0^j}{h} = (u_0^j)^2, \tag{13}$$

where the derivative $\partial u/\partial\xi|_{\xi=0}$ is replaced by a finite difference. We write the boundary condition (11) using the concentrations in four nodes, replacing the partial derivatives by the formulas

$$\left.\frac{\partial u}{\partial\Theta}\right|_{\xi=\alpha} \approx \frac{1}{\tau}(u_n^{j+1} - u_n^j), \quad \left.\frac{\partial u}{\partial\xi}\right|_{\xi=\alpha} \approx \frac{1}{2h}(u_n^{j+1} - u_{n-1}^{j+1} + u_n^j - u_{n-1}^j). \tag{14}$$

As a result we obtain a system of difference equations which, when we know the functions u_i^j at points of the j-th layer, enables us to find the values of u_i^{j+1} at the points of the subsequent j + 1 layer. This system was solved by the method of matching [6, p. 285]. An algorithm was devised for the computerized solution of the problem for cases of saturation and degassing with arbitrary values of the constants K, D, a. Important for the practical utilization of the results of the numerical solution of the problem of mass transfer is the choice of methods and criteria for comparing the theoretically calculated and the experimental values. For instance, for evaluating the kinetic characteristics K and D and the thickness of the boundary layer a from the experimentally obtained dependence of the mean gas concentration in the melt on time ($c_{ex}(t_i)$, i = 1, 2, ..., N) we can use the least squares method, considering the function

$$\Phi = \sum_{i=1}^{N} (c_{ex}(t_i) - c|_{x=a}(t_i, K, D, a))^2 w_i, \tag{15}$$

where $c|_{x=a}(t_i, K, D, a)$ is the value of the gas concentration at the boundary x = a at the instant t_i for the specified values of the constants K, D, a obtained from the solution of the problems (7)-(11). In the case of equally accurate measurements $w_i = 1$. The value of Φ is a function of the three variables K, D, a. To find the evaluations of the parameters K, D, a we have to find the minimum of the function Φ with respect to these parameters by known methods. Specifically, in the present work we carried out the minimization numerically on a computer using the gradient method of seeking the extremum.

The problem of finding two parameters characterizing the process of mass transfer during diffusion saturation of steel from experimental data was dealt with in [7] for an infinite medium with a linear boundary condition. For liquid metal these conditons are untypical.

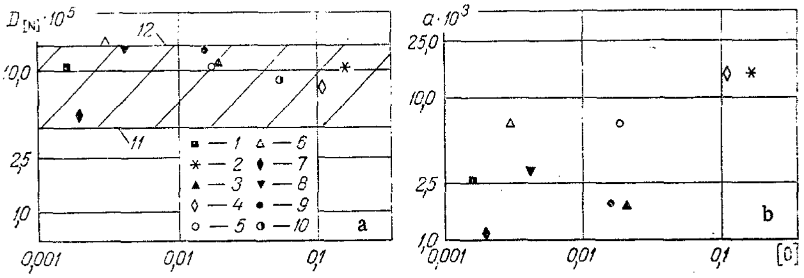

Fig. 2. Dependence of the diffusion coefficient of nitrogen (a) and of the thickness of the diffusion boundary layer in the metal (b) on the oxygen content of the melt (wt. %): 1-9) data of the present work Nos. 1-9 (see Table 1); 10) after [8]; 11) [9]; 12) [10]. [O], wt.%; a , cm; $D_{[N]}$, $cm^2 \cdot sec^{-1}$.

Moreover, the method of comparing the theoretical and the experimentally measured concentrations was not formulated in [7]. The accuracy of evaluating the sought parameters depends to a considerable extent on the choice of the method of comparison. The parameters K, D, and a were determined by the above-explained method from the experimentally obtained data on the kinetics of saturation with nitrogen and degassing in argon of iron melts with different content of dissolved oxygen under conditions of melting in the suspended state in an electromagnetic field with a frequency of 70 kHz. The content of metal is given in Table 1 in weight percent, the content of gas in volume percent. The weight of the liquid specimens was 2.6-2.8 g, the shape was close to spherical. The solution of the problem is also correct for a concave surface if the parameter a is much smaller than the radius of curvature. The shape of the specimen is taken into account in Eq. (5) by the ratio S/V. As an example Fig. 1 presents two series of experimental data and the theoretical curves describing them. The temperature and the composition during the experiment were constant with the exception of nitrogen in the metal. Altogether nine series of experiments were carried out. The results of their processing by the above-explained method are presented in Figs. 2 and 3.

In the general case the diffusion coefficient obtained by calculation from the data on mass transfer in the agitated metal may also contain a convective component. A comparison of this effective diffusion coefficient with the known coefficient of molecular diffusion makes it possible to evaluate the magnitude of the convective component of transfer in the direction toward the phase boundary. Here it must be taken into account that the diffusion coefficient obtained by calculation is less accurate than the coefficient of molecular diffusion measured by special methods. The values of the effective $D_{[N]}$ calculated by the described method are in satisfactory agreement with the value of the coefficient of molecular diffusion of nitrogen (see Fig. 2a). The dashed area in Fig. 2a is bounded by the minimal and maximal values of the coefficient of molecular diffusion according to the most reliable data of [9, 10]. It was established in [11, 12] that the presence of oxygen in iron has practically no effect on the magnitude of the coefficient of molecular diffusion of nitrogen. The calculated values of $D_{[N]}$ do not reveal any noticeable change upon increased oxygen content of the melt either (Fig. 2), regardless of the substantially reduced speed of sorption of nitrogen and the lower constant of the speed of the surface reaction K in consequence of the predominant adsorption of oxygen on the surface (Fig. 3). The data on mass transfer also contain information on the hydrodynamic structure of the liquid. The coincidence in magnitude and nature of the obtained value of the effective diffusion coefficient of nitrogen with the coefficient of molecular diffusion, measured by special methods, in dependence on the oxygen content show that the mechanism of mass transfer to the gas—metal interface is molecular and that the adopted model is physically substantiated. In view of the high sensitivity of the speed of mass transfer at large Prandtl numbers to the existence of turbulent motion, it may be concluded that turbulent pulsations near the gas—metal interface are attenuated, regardless of the considerable reduction of surface tension of iron at 1600°C: from 1750 to 900 mN/m when the oxygen content changes from 0.0015 to 0.15% [13, p. 94]. After the molecular mechanism of transfer has been established, it is expedient to repeat the calculations and to use tabulated values of the diffusion coefficient D and retaining as unknowns the parameters K and a . The accuracy of their determination thereby increases.

In our experiments the oxygen content and the speed of sorption of nitrogen depending on it varied within wide limits. The authors of [8] used high-frequency heating with a frequency of 400 kHz, weight of the metal 1.25 g. At the same time it may be expected that the

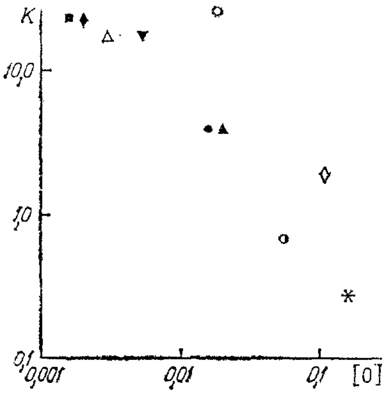

Fig. 3. Dependence of the constant of the speed of the surface reaction on the oxygen content of the metal. For notation see Fig. 2. K, $cm^4 \cdot g^{-1} \cdot sec^{-1}$.

agitation of the liquid metal will be less intense. Nevertheless, as was shown above, the calculated values of $D_{[N]}$ agree well with the known data, the magnitude of the parameters K and a and their dependence on the oxygen content also correspond well to the available a priori information. The values of K and D calculated after [8] coincide with our data (Figs. 2 and 3), and the value of a, as was to be expected, is one order of magnitude larger. The mean deviation of the calculated value of $D_{[N]}$ from the data of [11] was 43%, the maximal deviation was 88%. After repeated calculations using the known values of $D_{[N]}$ from [11] we obtained more accurate values of K and a whose deviations from the results of the first calculation with three unknown parameters were: mean one 9 and 35%, maximal one 20 and 46%, respectively. All these results indicate that in this case the solution of the inverse problem is correct.

The method under consideration is not only applicable to liquid metals but to other liquids, too. It makes it possible to obtain indirect information on the structure of flow, on the turbulization of a phase boundary from data on mass exchange.

NOTATION

D, diffusion coefficient of the gas; c, running gas concentration in the melt; x, distance from the gas–metal interface; t, time; K, constant of the speed of the surface reaction; a, thickness of the boundary layer; M, mass of the gas; S, area of the gas–metal interface; V, volume of the melt, c_0, c_e, initial and equilibrium gas concentration in the melt, respectively; u, ξ, Θ, dimensionless variables; α, γ, u_0, coefficients; h, τ, steps of the grid along the axes; i, j, number of steps; c_{ex}, experimental value of the mean gas concentration in the melt; N, number of experimental points in the series; w_i, weight with the change of error of measurements in time taken into account; $D_{[N]}$, diffusion coefficient of nitrogen.

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HEAT EXCHANGE AND RESISTANCE IN CHANNELS CONTAINING A POROUS FILLER

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The heat exchange and friction in pumping air through channels containing a porous filler (PF) consisting of pellets or wire pieces with different dimensions and thermal conductivity values are investigated in a wide range of porosities.

Heat exchange in channels is intensified considerably if the channels are obstructed with a porous, permeable heat-conducting filler, where perfect contact exists between the filler elements and between the latter and the channel walls. The heat from the channel walls is transmitted to the PF by the thermal conductivity λ_f of the porous filler body and is dissipated in the coolant over the entire transverse cross-section of the channel as a result of the intensive interstitial, convective transfer h from the heat-exchange surface that has been magnified by the factor F. For perfect contact between the PF and the channel walls, the analytical solution [1] indicates that the relationships between the thermal conductivity of the filler λ_f and of the coolant λ play the determining role in heat exchange intensification, while the heat exchange between the coolant and the boundary surface in the channel depends on λ_f/λ, the flow conditions Re_D, the extent X/D of the channel measured from the PF inlet, and the convective transport intensity h. Measurements [2, 3] in channels filled with steel wire PF, sintered and soldered to the channel walls, have shown that heat transfer to a single-phase flow increases by more than one order of magnitude for a PF porosity of less than 80%. At the same time, it was found in [2] that there is a more significant increase in the hydraulic resistance. The results of heat transfer measurements [3], while agreeing qualitatively with the solution obtained in [1], differ from it by 30-60% and reveal an additional effect of porosity. In [4], the increase of hydraulic friction in PF is related to inertial ($\beta\rho V^2$) and viscosity ($\gamma\mu V$) effects in porous channels; it is adequately generalized by the Darcy solution. The empirical quantities λ_f, h, β, and γ, which constitute individual characteristics of PF's [4, 5], are determined with considerable errors, which complicates the use of the solutions from [1, 4] for engineering predictions.

In many cases in practice, fastening of the PF elements to each other or to the channel walls is precluded by the specific features of the operating process or by technological constraints. In such channels, transverse heat transfer to the flow core directly from the channel walls by thermal conductivity of the PF either is attenuated or does not occur at all. However, it should be expected that, in spite of the absence of perfect contact among the PF elements or with the channel walls, there would be considerable intensification of heat ex-

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