NOTATION

$\bar{T}$, temperature, $T = (\bar{T} - T_W)/T_0$, dimensionless temperature; $\bar{C}$, concentration of absorbate in solution (mass fraction); T_W, wall temperature; d, b, constants determining state of saturation on liquid–vapor interface; $C = (\bar{C} - dT_W - b)/C_0$, dimensionless concentration; $y = y'/\delta$; $x = x'a/v\delta^2 = (1/\mathrm{RePr}) \cdot (x'/\delta)$; $\mathrm{Le} = a/D$, Lewis number; $\mathrm{Pr} = \nu/a$, Prandtl number; $\mathrm{Re} = V\delta/\nu$, Reynolds number; a, thermal diffusivity; D, diffusion coefficient; r_a, heat of absorption; c_p, specific heat; λ, thermal conductivity; ν, viscosity; ρ, density of solution; g_h, g_m, dimensional heat and mass fluxes, respectively; $\bar{T}_{av}$, $\bar{C}_{av}$, average values of temperature and concentration over cross section of film; Q_{hs}, Q_{hw}, dimensionless heat fluxes through film surface and solid wall; Q_m, dimensionless mass flux through film surface.

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THEORY OF REACTION DIFFUSION FOR BODIES OF PLANE, CYLINDRICAL, AND SPHERICAL SYMMETRY

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A solution of the nonstationary Stefan problem is presented for bodies of plane, cylindrical, and spherical symmetry in application to processes of diffusion interaction between metals and a gaseous oxidative medium.

The kinetics of metal interaction with gases is usually studied (see [1], for instance) by gravimetric (by the change in specimen weight), volumetric (by the quantity of absorbed gas), metallographic (by the periodic measurements of the thickness of the reaction-product films), and calorimetric (by the quantity of heat liberated by the reaction) methods. Hence, specimens of a different geometric shape (plates, wires, spherical particles, etc.) were used in tests. In this connection, it is interesting to analyze the question of the influence of the geometric shape of the specimens used on the regularity of reaction diffusion. Some results of such an analysis based on an assumption of a stationary distribution of the reagent concentration in the product film are contained in [2-4]. This question is analyzed in this paper in the general case of nonstationarity of mass transfer through the reaction-product film.

§ 1. Statement of the Problem

Within the framework of the classical theory of reaction diffusion [5], which is based on the assumption of the limiting role of transfer of the gaseous reagent through the reaction-product film, the process is described by a nonlinear Stefan problem, which has the following form for bodies of finite size but different geometric shape

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{n}{x}\frac{\partial c}{\partial x}\right), \quad r \leqslant x \leqslant R, \tag{1.1}$$

$$t = 0 \quad c = c_1 - \frac{c_1 - c_2}{R - r}(R - x), \quad R - r = \varepsilon \ll R, \tag{1.2}$$

$$x = R \quad c = c_1, \tag{1.3}$$

$$x = r \quad c = c_2, \tag{1.4}$$

$$c_2 \frac{d(R - r)}{dt} = D \left.\frac{\partial c}{\partial x}\right|_{x=r}. \tag{1.5}$$

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Here n is the symmetry parameter of the domain, $n=0$ is a plate, $n=1$ is a cylinder, and $n=2$ is a sphere. Condition (1.2) corresponds to the existence of a thin film on the specimen surface at the initial instant.

The following assumptions were made in writing the system (1.1)-(1.5):

1) Dissolution of the reagent in the metal is not considered (the solubility of the gas in the metal is assumed to be zero, and the whole interaction reduces to the formation of the product film);

2) the change in specimen volume during film growth is not taken into account (the possibility of such an assumption while examining the interaction between metals and gases results from an analysis of results in [6]);

3) the coefficient of diffusion is assumed independent of the concentration of reagent.

It is easy to obtain

$$\Delta H_s = \frac{1}{R^n} \int_r^R x^n \Delta H(c)\, dx, \tag{1.6}$$

$$\Delta m_s = \frac{1}{R^n} \int_r^R x^n \Delta m(c)\, dx \tag{1.7}$$

for the quantity of liberated heat ΔH_s per unit specimen surface, and the mean surface increment in mass Δm_s due to the formation of the product film. A linear approximation for the quantities $\Delta H(c)$ and $\Delta m(c)$,

$$\Delta H(c) = \Delta H_1 - (\Delta H_1 - \Delta H_2) \frac{c_1 - c}{c_1 - c_2}, \tag{1.8}$$

$$\Delta m(c) = \frac{\Delta m_1}{c_1} c. \tag{1.9}$$

can be used to evaluate the integrals in (1.6 and (1.7). The relationship (1.8) results from calorimetric measurements on the carbidization and nitriding of transition metals [7] and reflects the presence of a linear nature of the dependence of the magnitude of the thermal effect of the reaction on the nonmetal concentration in the film within the limits of the homogeneity domain of the reaction-product phase.

The self-similar solution of the problem (1.1)-(1.5) is widely known (see [8], for instance) for plane symmetry. There are no such solutions for cylindrical and spherical symmetry. Hence, in order to obtain computational empirical formulas for the rate of film growth, the heat liberation, and gain in weight of specimens of different geometric shape, the system (1.1)-(1.7), converted to dimensionless form, was solved on an electronic computer. In dimensionless form (1.1)-(1.7) are rewritten as follows:

$$\frac{\partial \eta}{\partial \tau} = \frac{\partial^2 \eta}{\partial \xi^2} + \frac{n}{\xi} \frac{\partial \eta}{\partial \xi}, \quad 1 - Z \leqslant \xi \leqslant 1, \tag{1.10}$$

$$\tau = 0 \quad \eta = 1 - \frac{1 - \xi}{Z}, \quad Z = \varepsilon' \ll 1, \tag{1.11}$$

$$\xi = 1 \quad \eta = 1, \tag{1.12}$$

$$\xi = 1 - Z \quad \eta = 0, \tag{1.13}$$

$$\frac{dZ}{d\tau} = \frac{1}{\eta_0} \frac{\partial \eta}{\partial \xi}\Big|_{\xi = 1 - z}, \tag{1.14}$$

$$Q_s = \int_{1-Z}^{1} \xi^n (\eta + Q_0)\, d\xi, \tag{1.15}$$

$$\Pi_s = \frac{1}{1 + \eta_0} \int_{1-Z}^{1} \xi^n (\eta + \eta_0)\, d\xi. \tag{1.16}$$

Here

$$\eta = \frac{c - c_2}{c_1 - c_2}; \quad \tau = \frac{Dt}{R^2}; \quad \xi = \frac{x}{R}; \quad Z = \frac{\delta}{R}; \quad Q_s = \frac{\Delta H_s}{R(\Delta H_1 - \Delta H_2)};$$

$$\Pi_s = \frac{\Delta m_s}{R\Delta m_1}\ ;\ Q_0 = \frac{\Delta H_2}{\Delta H_1 - \Delta H_2}\ ;\ \eta_0 = \frac{c_2}{c_1 - c_2}.$$

§ 2. Kinetics of Diffusion-Layer Growth

In the quasistationary approximation ($\partial\eta/\partial\tau = 0$) it is easy to obtain

$$n = 0;\ 2\quad \dot{Z} = \frac{K_*(1-n)}{(1-Z)[(1-Z)^{n-1}-1]}, \tag{2.1}$$

$$n = 1\quad \dot{Z} = \frac{K_*}{(Z-1)\ln(1-Z)} \tag{2.2}$$

for the growth rate of the dimensionless film thickness Z from the system (1.10)-(1.14) for different geometric shapes, where $K_* = \eta_0^{-1}$ is the film growth-rate factor in the quasistationary mode.

Processing the results of the numerical solution of the initial nonstationary system of equations showed that in the general case the interaction law can be represented for the three shapes under consideration in the form

$$\dot{Z} = (\dot{Z})_* \varphi_n(Z,\ \eta_0). \tag{2.3}$$

Here $(\dot{Z})_*$ is the interaction law obtained in the quasistationary approximation [formulas (2.1) and (2.2)], and $\varphi_n(Z,\ \eta_0)$ is a function taking account of the effect of nonstationarity in the mass transfer through the reaction-product film. Numerical computations yield for the function φ_n

$$\varphi_n(Z,\ \eta_0) = \left(1.04 - \frac{0{,}226}{\sqrt{2\eta_0}}\right)^2 \left[1 + \frac{A_n}{\sqrt{2\eta_0}}\ln(1-Z)\right]. \tag{2.4}$$

For n = 0, 1, and 2 the coefficient A_n equals, respectively, $A_0 = 0$, $A_1 = 0.153$, $A_2 = 0.235$.

Therefore, taking account of nonstationarity in the mass transfer in the case of plane symmetry ($A_0 = 0$) reduces just to a change in the magnitude of the constant in the kinetic law of film growth. An additional function, dependent on the film thickness Z, appears for the other shapes.

The error in computing the film growth rate $\dot{Z}$ by means of (2.3) and (2.4) is presented in Table 1 and it does not exceed 5%. The formulas have been selected in the range $\eta_0 = 0.75$-10, which corresponds to a real change in the parameter η_0 resulting from an analysis of the metal–gas phase diagrams [9].

In the plane symmetry case, the time for the product film to reach the center (Z = 1) of the specimen τ_n^* results from (2.3) and (2.4) as

$$\tau_0^* = \frac{1}{2K_*\varphi_0(\eta_0)}. \tag{2.5}$$

Processing the results of the numerical computation for the cylindrical and spherical symmetry yields

$$\tau_1^* = 0.12 + 0.259\,\eta_0, \tag{2.6}$$

$$\tau_2^* = 0.10 + 0.177\,\eta_0. \tag{2.7}$$

The error in (2.6) and (2.7) does not exceed 2%.

Analyzing the results obtained, the following must be noted.

a) The dimensionless rate of film growth $\dot{Z}$ for a given geometric shape is a function of the single parameter η_0 which is the relative width of the domain of phase homogeneity of the reaction product. As $\eta_0 \to \infty$ (the domain of homogeneity is small), we have $\dot{Z} \to 0$. In this case a quasistationary mode of progress of the phenomenon can be expected in this case for fixed values of the concentration on the film boundaries. As $\eta_0 \to 0$ (large domain of homogeneity), $\dot{Z} \to \infty$ and the process is essentially nonstationary. Therefore, the possibility of a quasistationary approximation is governed by the magnitude of the parameter η_0. It can be assumed that for $\eta_0 > \eta_0^*$ the film-growth process is quasistationary, while it is nonstationary for $\eta_0 < \eta_0^*$. The value of η_0^* is given by starting from the magnitude of the accuracy required in computing $\dot{Z}$. It follows from (2.3)-(2.4) with not more than a 15% error in the rate $\dot{Z}$ that: n = 0 $\eta_0^* = 1.8$, n = 1 $\eta_0^* = 3.2$ (for values $Z \le 0.5$), n = 2 $\eta_0^* = 4.1$ ($Z \le 0.5$).

b) The geometric shape of the specimen exerts an essential influence on the form of the kinetic curves $\dot{Z}(Z)$. The dependences $\dot{Z}(Z)$ are presented in Fig. 1 for the three shapes under consideration, obtained by integrating the initial system of equations on an electronic computer. It is hence seen that if $\dot{Z}$ increases monotoni-

TABLE 1. Comparison of Results from Calculation of $|\dot{Z}|$ on an Electronic Computer and Using (2.1)-(2.4)

Parameters		Z	Velocity values $\|\dot{Z}\|$			Errors in formulas, %	
n	η_0		computer calculations	formula calculations (2.1), (2.2)	formula calculations (2.3), (2.4)	(2.1)	(2.3)
0	1	0,1	7,70	10	7,75	35	1
		0,3	2,6	3,33	2,58	28	1
		0,5	1,56	2,00	1,55	28	1
		0,7	1,1	1,43	1,11	30	1
	3	0,1	3,07	3,33	3,00	8,5	2
		0,3	1,01	1,11	0,98	10	2
		0,5	0,61	0,66	0,60	8,2	2
		0,7	0,43	0,48	0,428	11,6	0,5
1	1	0,1	8,02	10,5	8,00	29	0
		0,3	2,95	4,01	2,93	36	0,5
		0,5	2,03	2,89	2,00	42	1
		0,7	1,78	2,78	1,76	56	1
	3	0,1	3,12	3,46	3,11	11	0,3
		0,3	1,18	1,32	1,17	12	1
		0,5	0,827	0,95	0,810	14,5	1
		0,7	0,755	0,92	0,750	22,5	1
2	1	0,1	8,65	11,11	8,40	28	2,9
		0,3	3,40	4,76	3,38	40	0,5
		0,5	2,59	4,00	2,60	54	0,04
		0,7	2,62	4,76	2,66	82	1,5
	3	0,1	3,35	3,70	3,29	10,5	2,0
		0,3	1,37	1,59	1,36	16	0,7
		0,5	1,09	1,33	1,09	20	0
		0,7	1,18	1,59	1,20	35	1,5

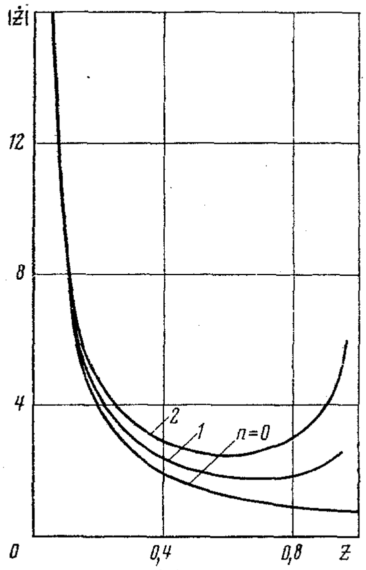

Fig. 1. The dependence $\dot{Z}(Z)$ for a plate, cylinder, and sphere for the value $\eta_0 = 1$.

cally for plane symmetry as Z grows (according to a parabolic law), then this quantity passes through a minimum for a cylinder and a sphere. In the limit case $Z \to 0$ (thin films), the kinetic curves for all three shapes are identical. An analysis of (2.3)-(2.4) shows that the limit values of the film thickness Z_*, for which the difference in the magnitudes of the rate $\dot{Z}$ for the cylinder and sphere does not exceed 15% compared to the plate, depend weakly on the parameter η_0 and in the range $\eta_0 = 1$-∞, equal, respectively, n=1, $Z_* = 0.30$-0.26; n= 2, $Z_* = 0.17$-0.13.

§ 3. Kinetics of Heat Liberation and Increase in Specimen Weight

In considering the regularities of heat liberation and the increase in specimen weight during reaction diffusion, it is expedient to perform an analysis of the phenomena in the quasistationary approximation before

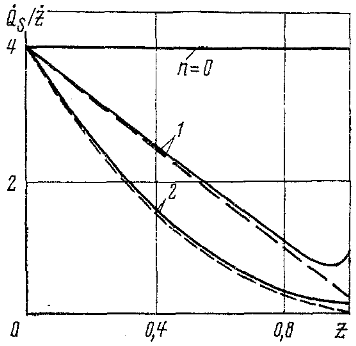

Fig. 2. The dependence of $\dot{Q}_S/\dot{Z}$ on Z for a plate, cylinder, and sphere for $Q_0=3.5$, $\eta_0=1$; solid lines correspond to a computation using (3.2) and (3.3) while the dashes correspond to a computation on an electronic computer.

executing a numerical computation on the electronic computer. In the quasistationary approximation case, the following results from (1.10)-(1.16):

a) For the rate of heat liberation $\dot{Q}_S$:

$$n=0 \quad \dot{Q}_s = \frac{1+2Q_0}{2}\dot{Z}, \tag{3.1}$$

$$n=1 \quad \dot{Q}_s = \frac{1}{2} f_1(\alpha,\ Z)\dot{Z}, \tag{3.2}$$

$$n=2 \quad \dot{Q}_s = \frac{1}{3} f_2(\alpha,\ Z)\dot{Z}; \tag{3.3}$$

b) for the rate of increase of specimen weight $\dot{\Pi}_S$:

$$n=0 \quad \dot{\Pi}_s = \frac{1+2\eta_0}{2(1+\eta_0)}\dot{Z}, \tag{3.4}$$

$$n=1 \quad \dot{\Pi}_s = \frac{1}{2(1+\eta_0)} f_1(\alpha,\ Z)\dot{Z}, \tag{3.5}$$

$$n=2 \quad \dot{\Pi}_s = \frac{1}{3(1+\eta_0)} f_2(\alpha,\ Z)\dot{Z}. \tag{3.6}$$

For the cylinder and sphere, the functions $f_n(\alpha,\ Z)$ here equal, respectively,

$$f_1 = 2\alpha(1-Z) + \frac{1-Z}{\ln(1-Z)} + \frac{1-(1-Z)^2}{2(1-Z)\ln^2(1-Z)},$$

$$f_2 = 3\alpha(1-Z)^2 + \frac{3}{2} - Z.$$

The parameter is $\alpha=Q_0$ in the expression for the heat-liberation rate, while it is $\alpha=\eta_0$ for the rate of specimen weight gain.

It is seen from the relationships (3.1)-(3.6) that if the ratio of the rate of heat liberation (specimen weight gain) and the film growth is a constant, then this ratio depends on the surface curvature for cylindrical and spherical symmetry: as the film thickness Z grows, the rate of heat liberation (specimen weight gain) diminishes more rapidly than the film growth rate. The nature of this dependence is shown in Fig. 2, where the results of a computation using (3.2) and (3.3) are compared with the data of a numerical integration on an electronic computer. In the limit case Z → 0, the expressions for the heat liberation rate and the gain in specimen weight agree for cylindrical and spherical symmetry with the relationship for a plate, which are written in dimensional form as

$$\frac{d(\Delta H_s)}{dt} = \overline{\Delta H}\frac{d\delta}{dt}, \tag{3.7}$$

$$\frac{d(\Delta m_s)}{dt} = \overline{\Delta m}\frac{d\delta}{dt}, \tag{3.8}$$

where $\overline{\Delta H} = (\Delta H_1 + \Delta H_2)/2$; $\overline{\Delta m} = [(c_1 + c_2)/2](\Delta m_1/c_1)$, i.e., in this case the resultant heat-liberation (weight gain) rate corresponds to the arithmetic mean value of the thermal effect of the reaction (weight gain) within the domain of phase homogeneity of the reaction products.

The results of a numerical computation of the initial system (1.10)-(1.16) on an electronic computer, some of which are illustrated in Fig. 2, exhibited good accuracy for the relations (3.1)-(3.6).

Therefore, for plane symmetry the kinetic equation in the heat liberation (gain in specimen weight) corresponds to a parabolic type, while the change in the heat-liberation (weight gain) rate is described by the relations (3.2), (3.3), (3.5), (3.6), (2.3), and (2.4).

In conclusion, let us note that in an experimental study of the kinetics of diffusion-layer growth on bodies of cylindrical and spherical symmetry, the universal kinetic information (independent of the characteristic size of the specimen) holds only up to definite values of the relative film thickness (the limit values of the thickness are presented in the text in the case of the cylinder and sphere). For thicker films, a passage to the limit to the characteristic body dimension $R \to \infty$ should be performed in the kinetic equation established experimentally.

NOTATION

c, nonmetal concentration in the film; c_1, c_2 values of the concentration at the upper and lower boundaries of the domain of product-film homogeneity; t, time; R, characteristic body dimension; r, coordinate of the film–metal boundary; δ, film thickness; D, coefficient of diffusion; ΔH_1, ΔH_2 heat of formation of one molar volume of MeX_y on the upper and lower boundaries of the homogeneity domain; Δm_1, Δm_2, mass increments corresponding to the nonmetal concentration in the film on the upper and lower boundaries of the homogeneity domain.

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