MODELING DIFFUSION DURING THE THERMOCYCLIC LOADING OF METAL

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Model representations of the diffusion of an impurity during heating are developed in a relaxational approximation based on the thermodynamics of irreversible processes. The calculations are compared with experimental data.

Structural changes in steel that improve its service properties and an increase in the mobility of its atoms during thermocyclic loading can be used to improve chemicothermal treatment processes [1-3]. It has been established experimentally that given the same overall time of diffusion saturation of steel specimens, the thickness of the resulting diffusion layer is considerably greater with the use of successive heatings and coolings of the metal than with isothermal holding [1].

Apart from accelerating diffusion, thermal cycling may influence the characteristic form of the concentration curves. Figure 1 shows certain characteristic distributions of carbon in the surface layers of specimens after thermal cycling. The distributions were obtained in a series of laboratory experiments and commercial trials of thermocyclic cementation and nitriding [3]. The temperature was changed by moving the charge containing the specimens from the hot chamber to the cold chamber or by changing the current supplied to the furnace heaters. The temperature was monitored with a chromel-alumel thermocouple embedded in the surface of the specimen. The chemical potential of the carbon in the gas phase was controlled with the aid of an electrochemical sensor by adding methane to the furnace gases. The carbon content of the surface layers of the metallic specimens was determined through layer-by-layer chemical analysis.

The experimental data was compared with estimates of carbon distribution through the specimen thickness obtained from the solution of parabolic [4] and hyperbolic [5] diffusion equations with boundary conditions of the third type. Here, the mass-transfer coefficient β^* was determined by a nonsteady method, while the effective diffusion coefficient was determined by the method recommended in [1] for thermocyclic cementation. For the regimes we examined, $\beta^* = 5.25 \cdot 10^{-8}$ m/sec and $D = 1.78 \cdot 10^{-11}$ m^2/sec. The relaxation times entering into the hyperbolic equation were found by numerical modeling on the basis of the best agreement between the theoretical relations and experimental data.

It is evident from the figure that the hyperbolic equation describes the empirical data considerably better than does the parabolic equation.

When a phenomenological approach is used, hyperbolic equations of heat conduction and diffusion are obtained as a result of allowing for relaxation in heat and mass transfer processes and the finite velocity of propagation of the thermal and concentration fronts [4-6]. Here, the diffusivity or diffusion coefficient and relaxation time that enter into the equations are phenomenological coefficients which are assumed to be known. If necessary, they can be found experimentally. The phenomenological description of transport processes is fairly inexact. A more detailed description requires the use of model representations of processes taking place at the level of the microstructure of the system. When diffusion in metals in the presence of strucutral defects was modeled in [7], the defects were assumed to have been macroscopic or point traps capable of absorbing atoms of a diffusing impurity and holding them for a certain period of time. This approach leads to diffusion equations of a

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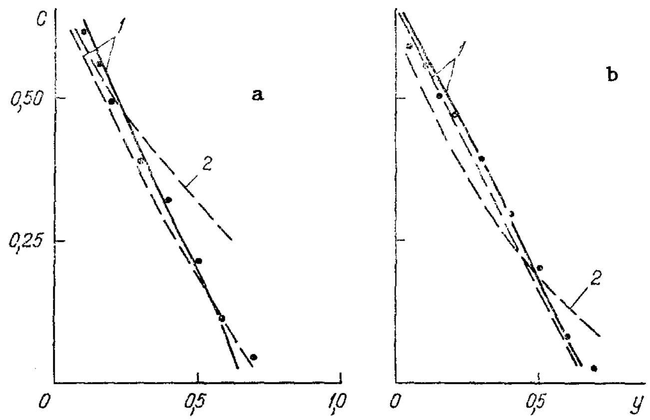

Fig. 1. Carbon concentration field after thermocyclic cementation with $T_{\text{furn}} = 910°C$, t = 4.67 h ($\beta = 1.259$, $\tau = 1.64$, $\tau_\xi = 1.024\ 10^4$ sec) (a) and $T_{\text{furn}} = 900°C$, t = 2.5 h ($\beta = 0.697$, $\tau = 2.87$, $\tau_\xi = 3.136\cdot 10^3$ sec) (b): 1) dashed curve — estimate obtained from (20); solid line — result obtained from the exact formula in [5]; 2) solution of the parabolic diffusion equation. y, mm.

more general form. The approximate character of the description in this case also leads to equations of the hyperbolic or elliptic type (depending on the relaxation times).

Thermocylic loading has its greatest effect on the material when phase transformations take place [1]. In this case, there is a change in the structure of the metal (refinement, reshaping, and reorientation of the grains), a change in the chemical or phase composition (such as the dissolution or precipitation of excess phases), and the creation and relaxation of internal stresses.

Thermocyclic loading which occurs with a complete phase transformation during the cementation of steels leads to an increase in the diffusional mobility of carbon by a factor of 2.5-3.0.

Proceeding on the basis of literature data and their own experimental results, the authors of [1] concluded that the acceleration of diffusion is due to the nonequilibrium state of the metal and features of its structure. There have been attempts to link the acceleration of diffusion with the creation of thermal stresses during thermal cycling. Several researchers have attributed the phenomenon of accelerated diffusion mainly to grain refinement and saturation of the metal by defects — vacancies and dislocations [2, 8-10].

The conclusion that vacancies and dislocations are in large part responsible for diffusion during thermocyclic loading is supported by the results obtained in [11-15] for isothermal conditions. Also, it follows from the survey [16] that there should be a sharp change in vacancy concentration during phase transformations. However, in the opinion of different authors, defects can both speed up and slow down diffusion [1]. All of these questions require further study. Thus, the wide range of phenomena accompanying diffusion and the impossibility of currently establishing a governing mechanism in the acceleration of diffusion during thermal cycling make it difficult to construct a rigorous quantitative theory that will account for the effect of all significant physical processes and, thus, all of the regime parameters in chemicothermal treatment on the diffusion saturation of metal by different elements.

Consequently, when developing mathematical models, it is interesting to consider phenomenological approaches based on the thermodynamics of irreversible processes and, in particular, its relaxational formalism [17, 18].

Using the approach taken in [19], we will examine the effect of thermal loads on diffusion. We will assume that a change in specimen temperature generates an internal process $\xi(t)$ in the metal which influences the diffusion of an impurity and obeys the kinetic equation

$$\frac{\partial \xi}{\partial t} = L_\xi A. \qquad (1)$$

Under isothermal conditions, $A = 0$, $\xi = 0$. Assuming as usual [17] that the entropy of the system depends on the parameters characterizing the equilibrium state and the quantity ξ – $s = s(u, c, \xi)$, and expanding s into a series in the neighborhood of temperature T^0 with second-order accuracy relative to the term containing ξ, $s = s^0(u, c) - 1/2g\xi^2$, where $g = -(\partial^2 s/\partial \xi^2)^0$, after differentitating s with respect to time t we obtain:

$$\frac{\partial s}{\partial t} = \frac{\partial s^0}{\partial u}\frac{\partial u}{\partial t} + \frac{\partial s^0}{\partial c}\frac{\partial c}{\partial t} - g\xi\frac{\partial \xi}{\partial t}. \qquad (2)$$

The partial derivatives in (2) are calculated at T^0 and can be found from Gibbs' fundamental equation $Tds = du - \mu dc$:

$$\frac{\partial s^0}{\partial u} = \frac{1}{T^0} = \vartheta^0, \quad \frac{\partial s^0}{\partial c} = -\frac{\mu^0}{T^0} = -\mu^0\vartheta^0. \qquad (3)$$

The local rates of change of the parameters obey the balance equation

$$\frac{\partial \varphi}{\partial t} = -\nabla \mathbf{J}_\varphi + \sigma_\varphi, \qquad (4)$$

where $\varphi = (s, u, c)$, $\mathbf{J}_\varphi = (\mathbf{J}_s, \mathbf{J}_u, \mathbf{J}_c)$.

Sources are absent, $\sigma_u = \sigma_c = 0$, from the balance equations for mass and internal energy. We will assume that the system allows the isolation of fast and slow variables [18], i.e., the inequalities $\tau_q \ll \tau_\xi < \tau_D$ exist for the characteristic times of diffusion and heat conduction in the internal process. The behavior of the system at times exceeding τ_q is determined by slower processes involving relaxation and diffusion [18]. This makes it possible to use the steady-state balance equation for internal energy $\nabla \mathbf{J}_u = \nabla \mathbf{J}_q = 0$ for the more rapid process of heat conduction. Thus, thermal loads influence diffusion through the internal process $\xi(t)$ with the generation of defects in the specimen. Having represented the entropy in (4) in the form $\mathbf{J}_s \approx \frac{\mathbf{J}_q}{T_0} - \frac{\mu \mathbf{J}_c}{T} = \vartheta^0 \mathbf{J}_q - \mu\vartheta \mathbf{J}_c$, after some elementary transformations we find the following expression from (2-4) for the entropy production

$$\sigma_s = -(\mu\vartheta - \mu^0\vartheta^0)\nabla \mathbf{J}_c - \mathbf{J}_c \nabla(\mu\vartheta) - g\xi\frac{\partial \xi}{\partial t}. \qquad (5)$$

For diffusion under isothermal conditions, $\xi = 0$. Thus, it is quite natural in a linear approximation to put $\mu\vartheta - \mu^0\vartheta^0 = \gamma\vartheta^0\xi$. With allowance for the last relation, entropy production (5) takes the form

$$\sigma_s = -\gamma\vartheta^0\xi\nabla \mathbf{J}_c - g\xi\frac{\partial \xi}{\partial t} - \mathbf{J}_c\nabla(\mu^0\vartheta^0 + \gamma\vartheta^0\xi). \qquad (6)$$

In accordance with the Curie principle, Eq. (6) leads to linear phenomenological laws for the vector process of diffusion and the scalar internal process characterized by the parameter $\xi(t)$:

$$\mathbf{J}_c = -L\vartheta^0\nabla(\mu^0 \times \gamma\xi), \qquad (7)$$

$$\frac{\partial \xi}{\partial t} = -L_\xi g^{-1}\xi - \gamma\vartheta^0 g^{-1}\nabla \mathbf{J}_c. \qquad (8)$$

Equation (8) is a special case of (1) in which the quantity A is expanded into a series in ratios of the parameters of the initial state with the temperature T^0. The increase in the diffusion coefficient during thermocyclic treatment was explained in [9] as being due to the interaction of atoms with vacancies $-D = D^0(1 + \xi)$, where ξ is the vacancy concentration. The rate of change of ξ is described by an equation similar to (8). Here, the terms on the right side play the role of vacancy sources and sinks. The authors of [9] numerically integrated the local vacancy balance equation together with the equations expressing the diffusion of impurity atoms and vacancies. The diffusion problem examined below is reduced to a single equivalent equation.

Since the quantity ξ in (7) characterizes the contribution of the internal process $\xi(t)$ to the chemical potential, $\nabla \mathbf{J}_c$ in (8) is a certain function of the concentration of diffusing atoms $\vartheta^0\nabla \mathbf{J}_c = \varphi(c)$, $L_\xi g^{-1} = \tau^{*-1}$, τ is the relaxation time. Considering this and having subjected (7) and (8) to Fourier transformation with respect to t (and keeping the same notation for the transforms as for the original), we obtain (7) without modification and we replace (8) with the expression

$$(1+i\omega\tau^*)\xi=\gamma\tau^* g^{-1}\varphi. \tag{9}$$

Having excluded ξ from (7) by means of (9), we find

$$\mathbf{J}_c=-L\vartheta^0\nabla(\mu^0+\gamma^2\tau^* g^{-1}\varphi/(1+i\omega\tau^*)).$$

If we consider that $\nabla\mu^0=\left(\frac{\partial\mu}{\partial c}\right)^0\nabla c,\ \nabla\varphi=\left(\frac{\partial\varphi}{\partial c}\right)\nabla c$, the flux can be represented in the form of Fick's law with an effective diffusion coefficient

$$\mathbf{J}_c=-D\nabla c,\quad D=D^0\left[1+\frac{\delta}{(1+i\omega\tau^*)}\right],\ D^0=L\vartheta^0\frac{\partial\mu^0}{\partial c},$$
$$\delta=\frac{\gamma^2\tau^*}{g}\left(\frac{\partial\varphi}{\partial\mu}\right)^0. \tag{10}$$

The same expression for the diffusion coefficient D(ω) can be obtained by using the operator representation introduced in [20]. We will henceforth examine the simplest case, when D^0 is independent of c. Using (10) in the mass balance equation (4), written for the Fourier transforms $i\omega c=-\nabla\mathbf{J}_c$, we find

$$i\omega c+(i\omega)^2\tau^* c=D^0(1+\delta+i\omega\tau^*)\nabla^2 c. \tag{11}$$

Considering that $(1+i\omega\tau^*/(1+\delta))^{-1}\simeq 1-i\omega\tau^*/(1+\delta)$, and limiting ourselves in the left side of (11) to terms that are quadratic with respect to ω, we change this equation to the form

$$i\omega c+(i\omega)^2\tau^*\frac{\delta}{1+\delta}=D^0(1+\delta)\nabla^2 c. \tag{12}$$

Having designated $\tau^*(\delta/1+\delta)=\tau_\xi$ and returning to the originals, we obtain the hyperbolic diffusion equation

$$\frac{\partial c}{\partial t}+\tau_\xi\frac{\partial^2 c}{\partial t^2}=D^0(1+\delta)\nabla^2 c. \tag{13}$$

As was already noted, another approach to describing diffusion in the interaction of atoms with defects is based on representation of the defects as macroscopic or point traps [7]. The kinetics of mass transfer on the surface of a trap is described in accordance with the classical theory of Smolukhovskii with allowance for the effect of relaxation processes on the capture and emission of impurity atoms by traps. The effect of the details of this mechanism on the macroscopic diffusion process is studied by means of self-consistent field theory. Description of the absorption and emission of diffusing atoms by defects in a relaxational approximation leads to an elliptical or (as in the case examined above) hyperbolic equation of unsteady diffusion. Here, the type of equation which results depends on the relaxation times. The exact solution obtained in [5] for (13) for a semi-infinite body with boundary conditions of the third type is quite complex in form and contains modified Bessel functions, thus requiring the use of numerical methods for practical calculations. It is therefore interesting to consider simpler approximate solutions that can be found by variational methods [21, 22]. Steady-state values (δI = 0) of the functional

$$I=\iint\limits_{\tau\,x}\left[C\frac{\partial C^0}{\partial\tau}-\frac{1}{2}\left(\frac{\partial C}{\partial\tau}\right)^2-C\frac{\partial^2 C^0}{\partial x^2}\right]dx\,d\tau, \tag{14}$$

where C^0 is a nonvarying function which after variation is identified with the sought $C=C^0$, correspond to the Euler–Lagrange equation

$$\frac{\partial C}{\partial\tau}+\frac{\partial^2 C}{\partial\tau^2}=\frac{\partial^2 C}{\partial x^2}, \tag{15}$$

which is represented by dimensionless expression (13) for a unidimensional problem. Here, $C=(c-c_0)/(c_g-c_0),\ x=y/\sqrt{D\tau_\xi}=y/\sqrt{D^0(1+\delta)\tau_\xi},\ \tau=t/\tau_\xi$.

We will examine the function $C=\exp[-\alpha^*\tau]f(x)$ as a test function. Inserting it into (14) and varying f, we obtain

$$\delta I=-\int_{\tau}\int_{x}\left[\frac{\partial^2 f^0}{\partial x^2}+\alpha^*(1+\alpha^*)f^0\right]\exp[-2\alpha^*\tau]\,\delta f dx d\tau=0, \tag{16}$$

from which follows the equation to determine $f(x) = f^0$:

$$\frac{d^2 f}{dx^2}+\alpha^*(1+\alpha^*)f=0. \tag{17}$$

With allowance for the solution of this equation and the choice of test function when $\alpha = -\alpha^* < 0$, we have

$$C(x,\ \tau)=\beta\frac{\operatorname{sh}[\sqrt{\alpha(1-\alpha)}(\tau-x)]}{\sqrt{\alpha(1-\alpha)}\operatorname{ch}[\sqrt{\alpha(1-\alpha)}\tau]+\beta\operatorname{sh}[\sqrt{\alpha(1-\alpha)}\tau]}. \tag{18}$$

In determining the constant of integration in (17), we used the condition at the front $C(x, \tau)_{x=\tau} = 0$ and a boundary condition of the third type on the surface of the specimen

$$\left(\frac{\partial C}{\partial x}\right)_{x=0}=\beta[C(0,\ \tau)-1]. \tag{19}$$

In the case of small values of the argument ($\operatorname{ch} z \simeq 1$, $\operatorname{sh} z \simeq z$), the simple relation below follows from (18)

$$C(x,\ \tau)=\frac{\beta}{1+\beta\tau}(\tau-x). \tag{20}$$

Variational methods can also be used to determine the correction factor. It should be noted that (20) coincides with the zeroth-approximation function when the diffusion equation is solved by the Shvets method [23].

Figure 1 shows experimental data on the carbon distribution through the specimen thickness as a result of chemicothermal treatment. The results are compared with the results of calculations by approximate formula (20) and results obtained on the basis of the exact solution of (15) in [5]. It is evident that both the exact and the approximate solutions of hyperbolic equation (15) describe the experimental data better than does the commonly-used parabolic equation. Highly-simplified formula (20) approximates the experimental data with an accuracy sufficient for practical purposes.

Changing over in (20) to dimensional variables

$$\frac{C-C_0}{C_g-C_0}=\frac{\beta^*}{\sqrt{D\tau_\xi}+\beta^*\tau}(t-y/\sqrt{D/\tau_\xi}), \tag{21}$$

we obtain a simple relation between parameters of the model which allows the parameters to be estimated on the basis of experimental data.

In conclusion, we note that instead of the linear relation $\mu\vartheta-\mu^0\vartheta^0=\vartheta^0\gamma\xi$ we can use the more general relation $\mu\vartheta-\mu^0\vartheta^0=\gamma^* A$, where the quantity A depends on the thermal stresses which develop in the specimen. Thus, the model constructed above can be refined by using available data on the connection between defect concentration and stresses. Another important problem is making the model account for regime parameters of the thermocyclic treatment – the number of cycles, their duration, and the duty factor.

NOTATION

ξ, relaxation parameter; A, affinity; $g = -(\partial^2 s/\partial\xi^2)^0$, quantity introduced in (2), u, internal energy; c, impurity concentration; μ, chemical potential of impurity; σ_s, entropy production; c_p, heat capacity; J_s, J_u, J_c flows for entropy, heat, and the impuritiy; τ_q, τ_ξ, τ_D, characteristic times of the processes of heat conduction, relaxation, and diffusion, respectively.

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EFFECT OF RE-EVAPORATION ON THE UNIFORMITY OF THE THICKNESS OF A FILM

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With complex kinematics characterizing the motion of the evaporator–substrate system, numerical modeling is used to study the effect of re-evaporation on the distribution of film thickness on the substrate.

The application of thin coatings by evaporation and condensation in a vacuum is usually done at pressures at which it is possible to ignore collisions among the molecules of the material being deposited and between these molecules and molecules of the residual gases. In such a free-molecular regime, the thickness of the film formed at point p of the substrate during the time τ is determined by the expression [1]:

$$d_p(\tau) = \frac{1}{\rho_I}\beta\frac{dm}{d\tau}\int\limits_0^\tau \frac{\cos\varphi_p(t)\cos\psi_p(t)}{\pi r_p^2(t)}\,dt = \frac{1}{\rho_I}\beta\frac{dm}{d\tau}U_p, \tag{1}$$

where ϕ_p and ψ_p are the angles of evaporation and condensation; $dm/dt = S_I\rho_I c_I \exp(-M_I L_I/RT_I)$ is the rate of removal of material from the surface of the evaporator; R is the gas

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