MODEL OF DIFFUSION SATURATION OF HETEROGENEOUS METALS

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The article deals with mass transfer from the surface into interstitial solid solution when in the bulk there are distributed traps able to retain diffusing admixtures. Explanations are given for the effects observed in the carburization of steel under conditions of variable temperature.

The most important service characteristics of metals and some other solid materials (ductility, hardness, wear resistance, impact toughness, etc.) can be substantially improved by saturating their surface layers with admixtures (carbon, nitrogen) forming interstitial solid solutions. The effectiveness of the respective processes of thermochemical treatment of such materials is determined in the final analysis by the macrokinetics and the characteristics of diffusional penetration of the admixtures into the solution from the adsorption layer that is in contact with the gaseous phase of adequate composition.

It was noted that a change of temperature in the course of the treatment (e.g., heat cycling) can considerably speed up the treatment and improve its final results [1, 2]. Here the concentration of the interstitial atoms in the surface layer of a real metal proves to be even higher than the values expected in an ideal homogeneous metal when the process is carried out under isothermal conditions with the maximal temperature of the cycle. The thickness of the diffusion layer in successive repeated heating and cooling of the metal may also exceed the dimensions of the diffusion zone in isothermal treatment. Improvement and choice of the optimal parameters of thermochemical treatment, effected at present on a purely empirical basis, require understanding of the physical mechanisms and causes of such a strong influence of the temperature regime; this is also the subject of the present work.

Attempts to interpret the numerous experimental data were connected with the hypotheses on the change of nature of mass transfer in comparison with ordinary linear diffusion in a concentration field. For instance, into the parabolic equation of diffusion a diffusion coefficient was introduced which depended on the temperature, the concentration of the admixture, and on the phase state of the metal, effects of thermodiffusion were taken into account, a boundary condition of third kind on the surface of the metal was imposed, the telegraph equation was used (see, e.g., [1-5]). In spite of the inaccuracy of the derivation of the equations in some of these publications, by empirical choice of the introduced coefficients it is possible to improve the formal agreement between experimental and theoretical data. However, on the whole the mechanisms of the phenomena remain unclear as before, and the results of such a comparison are unconvincing.

On the other hand there are many testimonies that the concentration of admixture in extended regions of the surface layer is higher than the limit concentration, i.e., the maximally possible concentration with the specified composition of the gaseous phase. As an example, Fig. 1 shows characteristic distributions of carbon concentration obtained in experiments of Kirnos et al. with nitriding of steel described in [5]. Obviously, no change of either the type of equation of mass transfer or of the boundary condition on the surface can in principle describe the above-mentioned effect. Its cause can only be some reservoirs (traps) in the bulk, able to absorb and conserve the diffusing admixture.

In real metals there are large numbers of microscopic inhomogeneities that are grains of another phase, micropores and vacancies, impurities, various structural defects which in principle may act as such traps. Notions of a general nature concerning the connection between accelerated diffusional transfer in heat cycling and the saturation of metal with defects due to the influence of the thermal stresses thus induced (in particular crumbling of the grains) were suggested, e.g., in [6, 7].

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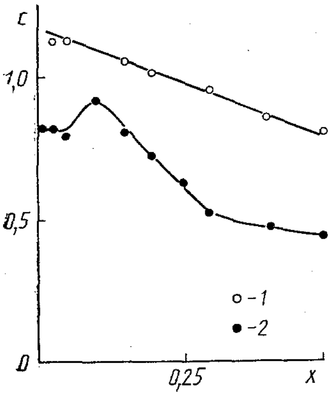

Fig. 1. Characteristic distributions of the carbon concentration over the depth of steel specimens after time t of nitriding in the regime of variable temperature: 1) seven cycles at T = 880-915°C, t = 325 min, $c_s(T) = 0.79\text{-}0.89\%$; 2) one cycle, T = 800-950°C, t = 40 min, $c^\circ = c_s(T_{max}) = 1\%$.

On account of the enormous variety of possible types of traps it would be senseless to go too much into the details of their properties in constructing the initial formalized model of the phenomena under discussion. Having in mind the fundamental aspect of the matter, we use here a number of simplifying assumptions which do not affect the qualitative aspect of these phenomena. We will deal, in particular, with metal containing uniformly distributed traps whose full bulk concentration is $\rho \ll 1$. For the sake of simplicity we assume that the dimension and absorptive capacity of the traps do not depend on the amount of admixture already absorbed, and that the diffusion flux to each of them from the matrix phase can be described in quasisteady approximation. Then the unidimensional equation of mass transfer can be written in the simple form [8]:

$$\frac{\partial c}{\partial t} + \frac{3\rho}{a^2}(c - c_*) = D\frac{\partial^2 c}{\partial x^2}, \tag{1}$$

while we neglect the dependence of D on ρ and c and identify it with the diffusion coefficient in the diluted solution. If the process is limited by diffusion, then for c we have to specify on the surface a boundary condition of the third kind with a mass transfer coefficient depending on the constants of the speed of the surface reactions [9, 10]. Considering, for the sake of determinacy, that this coefficient is large, we write

$$c|_{x=0} = c_s, \quad c|_{x\to\infty} \to c_i(\infty), \quad c|_{t=0} = c_i(x). \tag{2}$$

If $c < c_*$, and the traps do not contain a previously absorbed admixture, then the second term on the left-hand side of (1) has to be omitted.

The time of relaxation of the temperature fields is many orders longer than the time scale of diffusion. The temperature in the region that is of interest may therefore be regarded as uniform. In the general case we have to take into account at the same time the dependence of the coefficient D on T = T(t), the equilibrium concentration (in relation to the traps) of the admixture c_* in the matrix, and the surface value of the concentration c_s. Then (1) is an equation of parabolic type in which the dependence of the coefficients is specified by the temperature regime of the process of diffusion saturation. The solution of this equation with conditions (2) can be obtained numerically for any such regime.

Introducing the dimensionless variables

$$t = (L^2/D^\circ)\tau, \quad x = L\xi, \quad \{c,\ c_*,\ c_s,\ c_i\} = c^\circ\{\sigma,\ \sigma_*,\ \sigma_s,\ \sigma_i\}, \tag{3}$$

where D° and c° are some reference values of the diffusion coefficient and of the concentration, we rewrite (1) and (2) in the form

$$\frac{\partial \sigma}{\partial \tau} + \alpha^2(\sigma - \sigma_*) = \frac{\partial^2 \sigma}{\partial \xi^2}, \quad \alpha^2 = 3\rho\left(\frac{L}{a}\right)^2,$$
$$\sigma|_{\xi=0} = \sigma_s, \quad \sigma|_{\xi\to\infty} = \sigma_i(\infty), \quad \sigma|_{t=0} = \sigma_i(\xi). \tag{4}$$

If the process proceeds under isothermal conditions at the temperature T_1, it is natural to choose $D^\circ = D(T_1)$, $c^\circ = c_s(T_1)$; in that case $\sigma_s = 1$. For the sake of simplicity we assume

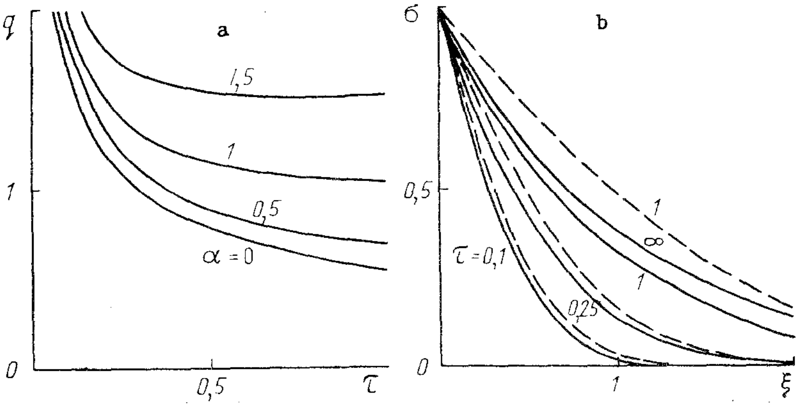

Fig. 2. Dependences q(τ) (a) and σ(ξ) (b) with $\alpha = 1$ and different τ (the numbers next to the curves): b) the dashed curves represent the solutions of the parabolic equation without absorption ($\alpha = 0$).

that the initial material did not contain admixtures either in the matrix or in the traps (and in particular, $\sigma_i = 0$) and that $\sigma_*(T_1) \approx 0$. Using Laplace transformation in (4), we obtain the following for mapping of concentration:

$$\sigma_p = p^{-1} \exp\left(-\xi \sqrt{p + \alpha^2}\right)$$

and for the original

$$\sigma = \frac{\xi}{2\sqrt{\pi}} \int_0^\tau \exp\left(-\frac{\xi^2}{4z} - \alpha^2 z\right) \frac{dz}{z^{3/2}} = \frac{1}{2}\left[e^{-\alpha\xi} \operatorname{erfc}\left(\frac{\xi}{2\sqrt{\tau}} - \alpha\sqrt{\tau}\right) + e^{\alpha\xi} \operatorname{erfc}\left(\frac{\xi}{2\sqrt{\tau}} + \alpha\sqrt{\tau}\right)\right]. \quad (5)$$

The dimensionless flux of matter from the surface is equal to

$$q = -\left.\frac{\partial\sigma}{\partial\xi}\right|_{\xi=0} = \frac{1}{\sqrt{\pi\tau}} e^{-\alpha^2\tau} + \alpha \operatorname{erf}(\alpha\sqrt{\tau}). \quad (6)$$

Values of diffusion without absorption in the traps, analogous to (5) and (6), are obtained after the passage to the limit $\alpha \to 0$, i.e.,

$$\sigma_0 = \sigma|_{\alpha=0} = \operatorname{erfc}\frac{\xi}{2\sqrt{\tau}}, \quad q_0 = q|_{\alpha=0} = \frac{1}{\sqrt{\pi\tau}}. \quad (7)$$

It is easy to show that for all α and τ the inequality $q > q_0$ is correct, i.e., the existence of traps leads to an increase of the amount of admixture penetrating into the metal. Specifically, with $\tau \to \infty$ we have $q \to \alpha$. Figure 2a shows the dependences of q on τ for different α in the region of small τ. Characteristic distributions of dimensionless concentration of admixtures in the matrix for situations with and without absorption are presented in Fig. 2b. It can be seen that absorption leads to steeper dependences of concentration on the coordinate; these are not so much characteristic of the parabolic rather than the hyperbolic equation of transfer, which explains to some extent the relative success attained with the aid of the latter in the interpretation of the experimental data [5].

With $\tau \to \infty$ we have $\sigma_0 \to 1$. To find the corresponding representation for σ, it is expedient to proceed directly from the map of this function with $p \ll \alpha^2$, when $\sigma_p \approx p^{-1}\exp(-\alpha\xi - p\xi/2\alpha)$, and, furthermore:

$$\sigma \approx \begin{cases} e^{-\alpha\xi}, & \xi < 2\alpha\tau, \\ 0, & \xi > 2\alpha\tau, \end{cases} \quad \tau \gg \frac{1}{\alpha^2}. \quad (8)$$

Thus, with $\tau \to \infty$ the distribution of the dimensionless concentration in the matrix tends to the distribution described by the steady-state function $e^{-\alpha\xi}$ in the interval $0 < \xi < \xi_*$,

$\xi_* = 2\alpha\tau$, which expands at constant speed with increasing τ. Outside this interval $\sigma \approx 0$. The magnitudes $\xi_*(\tau)$ can be regarded as the coordinates of the concentration front which propagates into the bulk of the metal. This is also a trait of some "hyperbolicity" of the process of transfer involving absorption. This last also causes large concentration gradients in the matrix which do not vanish as the process develops, and this also causes its acceleration, which is the more substantial, the more intensively absorption proceeds.

The dimensionless concentration of the admixture preserved in the traps, also attributable to c°, is equal to

$$s = \alpha^2 \int_0^\tau \sigma(\tau')\, d\tau'$$

and with long dimensionless times it can be represented in the form

$$s \approx \begin{cases} \alpha^2 e^{-\alpha\xi}(\tau - \xi/2\alpha), & \xi < 2\alpha\tau, \\ 0\quad , & \xi > 2\alpha\tau, \end{cases} \quad \tau \gg \frac{1}{\alpha^2}. \tag{9}$$

The distributions of σ and $\sigma + s$ in the surface layer at different instants are shown in Fig. 3a. They provide a perfectly natural explanation of the experiments in which the full concentration of the admixture in the bulk of this layer (usually determined with the aid of metallographic analysis) is higher than the surface concentration (see Fig. 1). With $\tau \to \infty$ $s \to \infty$ which, after all, has to do with the assumption that the traps have infinite capacity.

We now assume that the isothermal process at the temperature T_1 ends after time t_1 after which the temperature drops in a jump to the new constant value T_2. The diffusion of the admixture with $t > t_1$ is described by the equation for the concentration c' in the matrix, ensuing from (1), with the previous boundary conditions (2) and the initial condition $c' = c(t_1, x)$ with $t = t_1 = (L^2/D^\circ)\tau_1$, where $c(t_1, x) = c^\circ\sigma(\tau_1, \xi)$, and $\sigma(\tau_1, \xi)$ is determined from (6) or with $\tau_1 \gg \alpha^{-2}$ from (8). In the dimensionless variables (3), as before, we have the problem

$$\begin{gathered} \frac{\partial\sigma'}{\partial(\tau - \tau_1)} + \alpha^2 d(\sigma' - \sigma'_*) = d\frac{\partial^2\sigma'}{\partial\xi^2}, \quad \sigma' = \frac{c'}{c^\circ}, \quad d = \frac{D(T_2)}{D(T_1)}, \\ \sigma'|_{\xi=0} = m = c_s(T_2)/c_s(T_1), \quad \sigma'|_{\xi\to\infty} \to 0, \quad \sigma'|_{\tau=\tau_1} = \sigma(\tau_1, \xi). \end{gathered} \tag{10}$$

The diffusion coefficient, which depends on the temperature in accordance with Arrhenius' law, rapidly decreases with decreasing T in the temperature range that is of practical interest, and in any case, $d < 1$. In most cases the boundary value of the concentration $c_s(T)$, which is proportional to the solubility of the diffusing atoms in the metal [and consequently, also to m(T)], is an increasing function of T, i.e., $m < 1$. Both these values may be regarded as approximately known from experiments. However, since even the very nature of the traps, which play a certain role in the process of saturation, is unknown, we cannot say a priori anything about the function $c_*(t)$, and therefore about $\sigma_*(T)$ either.

We assume that the equilibrium concentration c_* increases with rising temperature, i.e., $\sigma_*' < \sigma_*$; then we may assume as before that $\sigma_*' \ll \sigma'$. In that case the traps continue as before to absorb the admixture, and when the temperature drops, the nature of the diffusion process changes only in the sense that part of the admixture contained at the instant t_1 in the direct vicinity of the surface diffuses, in view of the reduced surface concentration, at first to the adsorption layer: this explains the appearance of maxima in the concentration dependences of the type shown in Fig. 1. After some time the maximum in the concentration dependence vanishes, the direction of mass flow at the surface changes its sign, and the process of diffusion saturation continues at a somewhat lower rate corresponding to the new temperature.

A different situation arises when the equilibrium concentration decreases sufficiently rapidly with the temperature so that $c_*(T_2) \gtrsim c(t_1, x)$. In that case the traps continue absorbing the admixture in the region where $c(t_1, x) < c_*(T_2)$, i.e., with sufficiently small x. Conversely, with large x they release admixture as long as they either have not freed

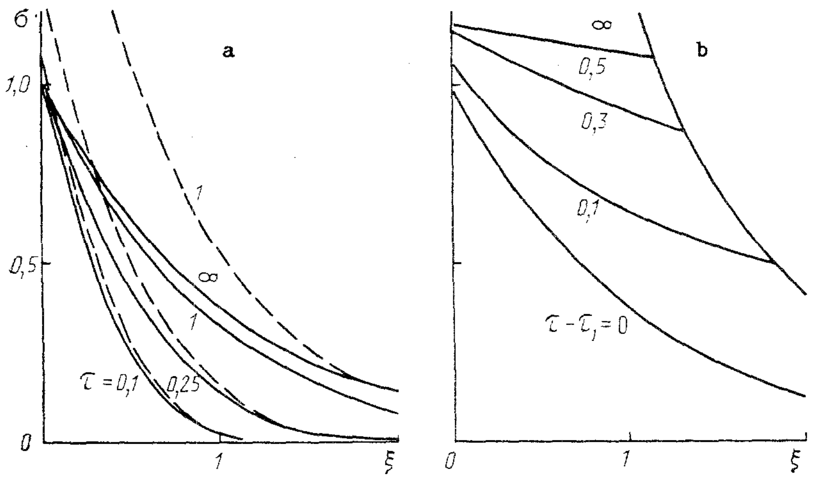

Fig. 3. Distributions of matrix and of full concentrations (solid and dashed curves, respectively) for $\alpha = 1$ with different τ (numbers next to the curves) (a) and the kinetics of the diffusionless establishment of the matrix concentration upon drop of temperature for $\alpha = 1$, $\tau_1 = 3$, $d = 0.25$, $m = 1.2$ and different $\tau - \tau_1$ (numbers next to the curves) (b).

themselves completely of the admixture, or the running value of c' at the point under consideration does not become equal to $c_*(T_2)$.

Applying Laplace transformation to (10), we obtain

$$d\,\frac{d^2\sigma_p'}{d\xi^2} = p\sigma_p' - \sigma(\tau_1,\ \xi) + \alpha^2 d\left(\sigma_p' - \frac{\sigma_*'}{p}\right), \tag{11}$$

$$\sigma_p'|_{\xi=0} = m/p,\quad \sigma_p'|_{\xi\to\infty} \to 0.$$

In case $\tau_1 \gg \alpha^2$ or if we neglect the possibility of voiding the traps, the solution of this problem has the form ($\xi < \xi_* \to \infty$):

$$\sigma_p' = \left(\frac{m}{p} - \frac{d\alpha^2\sigma_*' p}{p + d\alpha^2} - \frac{e^{-\alpha\xi}}{p}\right)\exp\left(-\sqrt{\frac{d\alpha^2 + p}{d}}\right) + \frac{d\alpha^2\sigma_*' p}{p + d\alpha^2} + \frac{e^{-\alpha\xi}}{p}.$$

The original of this expression describes the field $\sigma'(\tau,\ \xi)$ only in the region $\xi < \xi^*$, where $\xi^*(\tau)$ is the front separating the regions with occupied and vacant traps, which moves to the free surface. At an arbitrary point of the trap the entire accumulated admixture is released at the instant $\tau = \tau^*(\xi)$, where τ^* is the root of the equation $\xi = \xi^*(\tau)$. The problem of determining the fields of concentration with $\tau > \tau^*$ can be easily obtained from (10) by omitting in the equation the term describing the source or the sink. After some simple calculations we obtain in the region $\xi < \xi_*$ for $\tau_1 < \tau < \tau^*$:

$$\begin{aligned}\sigma' = \frac{m - e^{-\alpha\xi}}{2}\left[e^{-\alpha\xi}\operatorname{erfc}\left(\frac{\xi}{2\sqrt{d(\tau-\tau_1)}} - \alpha\sqrt{d(\tau-\tau_1)}\right) + e^{\alpha\xi}\operatorname{erfc}\left(\frac{\xi}{2\sqrt{d(\tau-\tau_1)}} + \alpha\sqrt{d(\tau-\tau_1)}\right)\right] - \\ - d\alpha^2\sigma_*'\int\limits_{\tau_1}^{\tau-\tau_1} e^{-d\alpha^2\tau'}\operatorname{erfc}\left(\frac{\xi}{2\sqrt{d\tau'}}\right)d\tau' + \left[1 - e^{-d\alpha^2(\tau-\tau_1)}\right]\sigma_*' + e^{-\alpha\xi}\end{aligned} \tag{12}$$

and for $\tau > \tau^*$

$$\sigma' = \frac{1}{2\sqrt{\pi d(\tau - \tau^*)}}\int\limits_0^\infty [\sigma'(\tau_*,\ \xi') - m]\left[\exp\left\{-\frac{(\xi-\xi')^2}{4d(\tau-\tau_*)}\right\} - \exp\left\{-\frac{(\xi+\xi')^2}{4d(\tau-\tau_*)}\right\}\right]d\xi' + m, \tag{13}$$

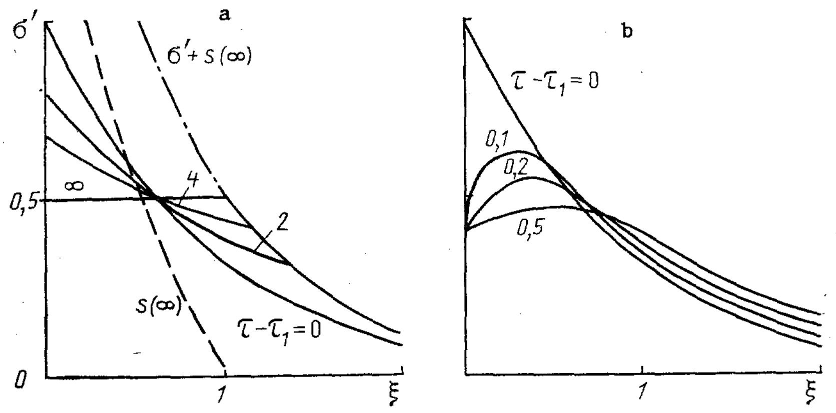

Fig. 4. Dimensionless concentration in the matrix after drop of temperature in diffusionless approximation (a) and with a view to diffusion (b) for $\alpha = 1$, $\tau_1 = 1$, $m = 0.5$, and $d = 0.25$; the numbers next to the curves give the values of $\tau - \tau_1$.

where the function $\tau^*(\xi)$ is determined by the equation

$$\int_{\tau_1}^{\tau_1+\tau^*} d\alpha^2 [\sigma'(\xi, \tau') - \sigma'_*]\, d\tau' + s(\tau_1, \xi) = 0. \qquad (14)$$

Using the simplest balance expressions we can also easily find the dependence on time and the coordinates of the concentration of the admixture preserved in the traps.

The zero approximation in the description of the exchange between the matrix and the traps can be obtained by simply neglecting diffusion at the temperature T_2. Then the solution of Eq. (10) becomes trivial. Figure 3b shows the distributions of concentration corresponding to different $\tau - \tau_1$ when the state with $\tau = \tau_1$ is described by one of the pairs of curves (see Fig. 3a), and $\sigma_*' > 1$ (i.e., all the traps release the admixture when $\tau > \tau_1$). The curves $\sigma'(\xi)$ have characteristic breaks when $\xi = \xi^*(\tau)$.

If the new equilibrium concentration $c_*(T_2)$ is lower than the old boundary concentration $c_s(T_1)$, then together with the region in which the matrix receives admixture from the traps, there appears another region directly adjacent to the surface in which the absorption of admixture by traps continues. Concentration curves for such a situation, analogous in sense to the curves presented in Fig. 3b, are shown in Fig. 4a. In the metal there appears a boundary layer within which the concentration of the admixture in the matrix tends to a constant value equal to the concentration $c_*(T_2)$.

After all, diffusion smoothes the concentration curves which in that case can be described with the aid of relations (12) and (13). Figure 4b shows the concentration profiles corresponding to relatively small $\tau - \tau_1$ for the same conditions as in Fig. 4a.

According to the developed model, the first high-temperature stage of the process involves saturation of the metal with a substance from the gaseous phase, at the second stage the admixture is released from the traps and the concentration in the matrix is equalized.

Thus, the notion of the existence of traps makes it possible in fact to explain many hitherto incomprehensible experimental facts if we assume that these traps absorb the admixture at high temperatures and release it at low ones. The other model assumptions concerning the properties of the traps as expressed above are not substantial in principle: the corresponding generalizations (which can be made, in particular, with the use of methods from [8]) only lead to a more complex mathematical formulation of the problems.

The cardinal problem consists in the adaptation of the model, i.e., in identifying the traps which really affect the processes of thermochemical treatment. The solution of this problem can apparently be obtained by confronting the theoretical expectations with the experimental data. This, however, is made difficult by two circumstances: firstly, that by far most of the experiments were carried out under fairly complex temperature regimes, and secondly, that an indispensable theoretical data bank is lacking. It is therefore necessary to set up simultaneously special experiments with simple temperature regimes (e.g., of the type discussed above) and to carry out a cycle of numerical calculations for these regimes with the use of accessible information on D(T) and $c_s(T)$ and appropriate model dependences for $c_*(T)$.

It should be emphasized that the results of such adaptation may turn out not to be very hope-inspiring. This possibility cannot be ruled out because physical reality is much richer and variegated than the simple model notions used above. After all, the most restrictive assumptions are those concerning the constancy of concentration and properties of the traps which in actual fact will hardly be realized. The suggested model should therefore be regarded merely as some preliminary stage in the fundamental solution of this fairly complex scientific and technical problem, and no more than that.

In the generalization and development of the model two basic circumstances have to be taken into account. Firstly, the number of traps may change in the course of the heat cycling process, both on account of thermal stresses, as pointed out above already, and as a result of the appearance or disappearance of nuclei of a new phase (the greatest effect induced by heat cycling is encountered in particular when it is carried out in the interval between the temperature ranges of existence of different phases, e.g., of ferrite and austenite in the heat treatment of steel). Secondly, it is possible that the size of the traps (of growing or dissolving elements of a new phase) changes substantially, and that consequently their ability to absorb the diffusing phase also changes. The analysis of these effects may be regarded as the natural direction in which the theory should be further developed.

NOTATION

a, radius of the traps; c, c_s, c_i, c_*, concentration of admixture and its boundary, initial, and equilibrium value, respectively; D, diffusion coefficient; d, m, magnitudes introduced in (10); L, linear scale of the process; p, parameter of the Laplace transform; q, dimensionless mass flow; s, dimensionless concentration in traps; T, temperature; t, time; x, coordinate; α, exchange coefficient introduced in (4); ρ, volume concentration of the traps; σ, dimensionless concentration of the admixture; τ, dimensionless time; ξ, dimensionless coordinate.

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