NONISOTHERMAL SATURATION OF A HETEROGENEOUS METAL WITH IMPURITY

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We consider the process of diffusive saturation with impurity atoms of metal from a surface in the presence of distributed traps over the volume able to capture and emit a diffusing impurity. The effect, exerted on mass transfer by an equilibrium characteristic of traps and by a rate of atomic exchange between a matrix and traps at variable temperature, is studied.

Diffusive penetration of atomic impurities from a gas phase into solids and, primarily, into metals is generally accompanied by an active interaction of diffusing atoms with a body substance and with its numerous structural defects, which gives rise to various phase and chemical transformations in the solid phase. The situation gets still more complicated, when the conditions of thermodynamic equilibrium in unsteady processes change. The latter occurs, for instance, with an application of variable temperature fields. Thermocyclic effects on the metal in a definite temperature interval induce structural alterations, an origination and relaxation of thermal stresses, and a generation of dislocations and nonequilibrium vacancies [1]. A wide range of real structural defects (foreign inclusions, elements of a new phase, micropores, grain boundaries, vacancies, etc.) and diversity of physicochemical mechanisms of the transformations developing on them bring about a number of effects new to diffusive transfer of the impurity in this case. Some of them (an increase in the total number of the impurity atoms in the metal and of a depth of the diffusion layer in thermal cycling as compared to those obtained in isothermal conditions) are widely used in working out new technologies for chemicothermal treatment of metal products in order to improve their working properties.

Presently, optimal parameters of the chemicothermal treatment are refined and selected on a purely empirical basis. Attempts to interpret extensive experimental data, associated either with introducing a diffusion coefficient dependent on a temperature, an impurity concentration, and a phase composition of the metal [1], or with taking into account thermal diffusion [2-4], and with considering relaxation processes, which lead to a hyperbolic diffusion equation [5], do not clarify mechanisms of the effects observed experimentally. Guided by analyzing experimental data and, specifically, the effect of the impurity accumulation up to concentrations higher than critical in the near-surface region of the metal, study [6] advanced a suggestion that there are certain defects (traps) in the metal, which are capable of absorbing and conserving a diffusing mixture. An analytical investigation of mass transfer in a medium containing traps at variable temperature allowed one to account for the above-stated effect and for the augmentation of the total amount of the impurity in the metal under the action of thermal cycling.

Study [6] examined transfer of the impurity atoms in the medium with traps on the premise of a high rate of impurity exchange between the matrix and the defects, such that a local equilibrium is set up at the defect boundary. However, the rate of atomic absorption and emission by the defects can in many cases be comparable to the rate of diffusive transfer of these atoms in the matrix. A variation in the kinetics of atomic interaction with the defects at variable temperature will, of course, affect the mass transfer process.

We consider nonisothermal saturation of a solid with isolated defects with the impurity atoms taking account of a finite rate of atomic exchange between the defects and the matrix. Since the isolated defects are enormously diverse, detailing their properties is superfluous. Therefore, we will model the defects, just as in [6], by spherical traps of radius a, which are able to capture and emit the diffusing mixture. We will also employ some simplifying assumptions having no effect on a qualitative aspect of the phenomena.

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Let us consider a metal with immovable uniformly distributed defects whose absorptivity is independent of the quantity of an impurity already absorbed (this holds for micropores, inclusions of a new phase, and chemical compounds), and whose volume concentration is $\rho << 1$. The latter allows one, when describing the atomic diffusion in the vicinity of each particle, to consider the defect located in a practically infinite medium, according to Smolukhovskii's classical method. We will model the kinetics of atomic exchange between the matrix and the defects by a first-order reaction. Then, in conformity with the general theory [7,8], a one-dimensional equation for the impurity concentration in the matrix is written in the form

$$\frac{\partial c}{\partial t} - 4\pi a^2 n \frac{\lambda D}{\alpha a + D}(c_* - c) = D\frac{\partial^2 c}{\partial y^2}, \tag{1}$$

where c_* is the impurity concentration in the matrix, which is equilibrium relative to the traps; D is the diffusion coefficient in the matrix; λ is the rate constant of atomic exchange between the matrix and the traps; and n is the numerical concentration of particles. An expression for the concentration of the impurity conserved in the traps is obtained from the material balance equation

$$c_{\text{л}} = 4\pi a^2 n \frac{\lambda D}{\lambda a + D}\int\limits_0^t (c - c_*)\, dt' + c^0_{\text{л}}. \tag{2}$$

When the spherical particles, playing the part of traps, are chemical combinations of the impurity atoms with the matrix atoms or with other species (carbides, nitrides, oxides, etc. for metals can exemplify such combinations), then, within the framework of the adopted assumptions, we have the following equation for the particle size variation

$$\gamma\frac{\partial a}{\partial t} = -\frac{\lambda D}{\lambda a + D}(c_* - c),$$

here γ is the impurity concentration in the particle governed by a composition of the chemical combination.

Disregarding a possible variation in the particle size ($\gamma >> 1$) and assuming that a rate of surface processes at the metal–saturating medium interface is high, such that a local equilibrium is established, we write the boundary and initial conditions for the impurity concentration field in the matrix as

$$c|_{y=0} = c_f, \quad c|_{y\to 0} \to c_i(\infty), \quad c|_{t=0} = c_i(y). \tag{3}$$

In the case, when $c < c_*$ and the defects are free from the impurity absorbed previously, the second term on the left side of Eq. (1) must be dropped.

Inasmuch as the relaxation time of temperature fields in metals exceeds a time scale of the diffusion by many orders of magnitude, it is natural to regard the temperature in the diffusion region in question as uniform. A time dependence for the coefficients entering into Eq. (1) (for the diffusion coefficient D and for the impurity concentration in the matrix c_*, which is equilibrium in relation to the traps) is assigned by a temperature mode of the saturation. The concentration at the surface c_f can in this case alter arbitrarily.

Let c_f = const and c_i = const. Having introduced the dimensionless variables $t = (L^2/D^0)\tau$, $y = L\eta$,

$$\{c,\ c_*,\ c_f,\ c_i,\ c_{\text{л}}\} = \{\sigma,\ \sigma_*,\ \sigma_f,\ \sigma_i s\}(c_f - c_i) + c_i,$$

where D^0 is a certain reference value of the diffusion coefficient and L is the characteristic linear scale, we recast Eqs. (1)-(3) in the dimensionless form

$$\frac{\partial\sigma}{\partial\tau} + \alpha^2(\sigma - \sigma_*) = \frac{\partial^2\sigma}{\partial\eta^2},$$

$$\sigma|_{\eta=0} = 1, \quad \sigma|_{\tau=0} = 0, \quad \sigma_* = \frac{c_* - c_i}{c_f - c_i}, \quad \alpha^2 = 4\pi a^2 n\frac{\lambda L^2}{\lambda a + D^0}, \tag{4}$$

$$s = s(\eta) + \alpha^2\int\limits_0^\tau (\sigma - \sigma_*)\, d\tau'.$$

Hereinafter we will restrict ourselves to the case with $c_f > c_i$ and $c_* > c_i$.

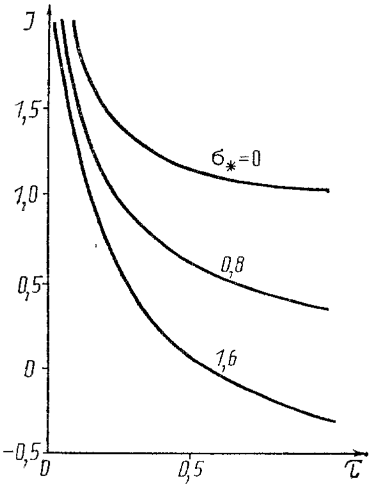

Fig. 1. Time dependence of dimensionless flux at the surface $\eta = 0$ in the material with defects for various values of concentration in the matrix σ_* which is in equilibrium in relation to the defects (number near the curves), $\alpha^2 = 1$.

Applying the Laplacian integral transform method to the problem (4), it is easy to find a dimensionless substance flux from the surface

$$J = -\left.\frac{\partial\sigma}{\partial\eta}\right|_{\eta=0} = \frac{1}{\sqrt{\pi\tau}}\exp(-\alpha^2\tau) + \alpha(1-\sigma_*)\,\mathrm{erf}(\alpha\sqrt{\tau}). \tag{5}$$

This expression for the flux corresponds to the impurity saturation of the material with defects for $\sigma_* = 0$ or $\sigma_* > 0$, when the defects contain a sufficient amount of the impurity by the initial time instant, such that Eq. (1), with the source term on the left side other than zero, is valid in the entire region over the process time under consideration.

Analyzing expression (5) makes it clear that in these conditions the impurity flux from the surface to the metal and, hence, the total amount of the impurity are larger for the material with defects, for which the thermal activity $c_*(\sigma_*)$ is smaller, i.e., $\partial J/\partial\sigma_* = -\alpha\mathrm{erf}(\alpha/\sqrt{\tau}) < 0$.

If the concentration at the surface c_f is higher than that at equilibrium relative to the defects c_*, then the metal gets saturated throughout the time interval with the impurity ($J \geq 0$), whose distribution between the material and the defects is a function both of $c_*(\sigma_*)$ and $\alpha^2(\lambda)$. Thus, notwithstanding a decrease in the total amount of the impurity in the metal with increasing $\sigma_* < 1$, the concentration in the matrix σ, which is a solution to the system (4), grows:

$$\sigma = \frac{1}{2}\left[\exp(-\alpha\eta)\,\mathrm{erfc}\left(\frac{\eta}{2\sqrt{\tau}} - \alpha\sqrt{\tau}\right) + \exp(\alpha\eta)\,\mathrm{erfc}\left(\frac{\eta}{2\sqrt{\tau}} + \right.\right.$$
$$\left.\left. + \alpha\sqrt{\tau}\right)\right] + [1 - \exp(-\alpha^2\tau)]\sigma_* - \alpha^2\sigma_*\int_0^\tau \exp(-\alpha^2\tau')\,\mathrm{erfc}\left(\frac{\eta}{2\sqrt{\tau'}}\right)d\tau'.$$

In the case with $c_* \geq c_f$ the impurity is emitted from the defects into the matrix in the entire region of nonempty traps. For small times of the process $J \geq 0$, i.e. the metal is saturated with the impurity. However, if there is a sufficient amount of the impurity in the defects, the emission leads to equalization of the impurity concentration over the matrix in the near-surface region of the metal, and subsequently to its increase as compared to the boundary value. Here the metal saturation is usually replaced by the metal depletion. In the limit, i.e., on the assumption that the defects contain an infinite amount of the impurity by the initial time instant, we obtain $J|_{\tau\to\infty}\ -\alpha(\sigma_* - 1)$. Figure 1 plots a time dependence of the dimensionless flux at the metal surface for various σ_*.

Let us examine the effect of the rate of atomic exchange between the matrix and the defects λ on the flux from the surface. With a possible emptiness of the defects neglected, the equality is true

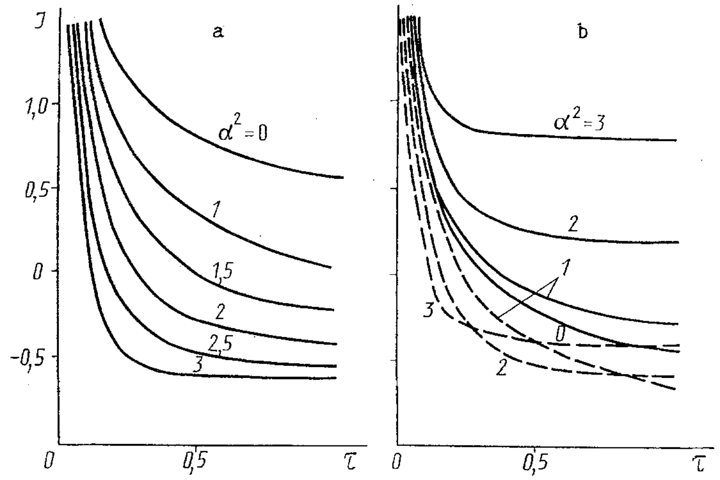

Fig. 2. Time dependence of dimensionless flux at the surface $\eta = 0$ for various α^2, characterizing the rate of atomic exchange between the matrix and defects: a) $\sigma_* = 1.2$; b) $\sigma_* = 0.4$ (solid curve) and 0.8 (dashed curve).

$$\frac{\partial J}{\partial \lambda} = \left[(1 - 2\sigma_*)\frac{2\alpha\sqrt{\tau}}{\sqrt{\pi}}\exp(-\alpha^2\tau) + (1 - \sigma_*)\frac{2}{\sqrt{\pi}}\int_0^{\alpha^2\tau}\frac{\exp(-u)}{2\sqrt{u}}du\right] * \\ * \frac{4\pi a^2 n L^2 D}{2\alpha(\lambda a + D)^2}. \tag{6}$$

Clearly, in the case $\sigma_* \geq 1$ (the impurity is emitted by the defects throughout the volume) an increase in the process rate causes a reduction in the flux across the surface.

If the impurity is absorbed by the defects in the near-surface region ($\sigma_* < 1$), then for $0 \leq \sigma_* < 1/2$ the impurity flux across the surface increases during the entire process with rising λ, whereas for $1/2 < \sigma_* < 1$ it diminishes with an increasing exchange rate at short times and grows at long times.

The latter regularity can be explained in the following way. A variation of the concentration in the matrix, specifying a flux at the boundary, near the surface $\eta = 0 + \delta$, $\delta << 1$ occurs through several factors, viz., through a decrease due to capture by the defects, and through a rise due to diffusion and emission from the defects. With short times, the boundary between the regions of atomic absorption and emission by the traps $\sigma = \sigma_*$ is close to the surface. The larger σ_*, the closer this boundary is to the metal surface and the stronger the influence of emission from the traps on a concentration gradient at the surface. Moreover, an increase in σ_*, roughly speaking, enhances the atomic emission and reduces the atomic absorption by the traps in relevant regions. Therefore, when $1/2 < \sigma_* < 1$, with increasing rate of exchange processes λ the concentration gradient in the near-surface region decreases because the emission and diffusion is stronger than that which grows due to the atomic absorption by the defects. Exactly this fact is responsible for the reduction in the flux across the surface at short times of the process. As the process evolves, the region of atomic absorption by the traps, which adjoins the surface, becomes larger, and absorption starts predominating over the concentration gradient at long times. A rise in the absorption rate causes an increase in the flux across the surface. Figure 2a shows a time variation of the dimensionless flux at the boundary with various $\alpha^2(\lambda)$ for $\sigma_* = 1$ and 2, and Fig. 2b plots analogous relations for $\sigma_* = 0.4$ and $\sigma_* = 0.8$.

It ensues from the above analysis that imposing variable temperature effects during diffusive saturation of the metal allows a control, to a considerable extent, both over the total amount of the impurity in the metal and over the impurity distribution between the matrix and the defects owing to the temperature dependence of thermal activity of the defects $c_*(T)(\sigma_*(T))$ and of the rate of atomic exchange between the matrix and defects $\alpha^2(T)(\lambda(T))$.

It is seen from the relationships, derived above without regard to the region with empty defects, that, with multiple instantaneous temperature variations, the effect of the impurity accumulation in the metal with defects is stronger in the case when the temperature dependences for $\sigma_*(T)$ and $\lambda(T)$ are opposite in character than when they are of the same character. The first case corresponds to the situation, when the defects absorb the impurity at a higher rate with one temperature than they

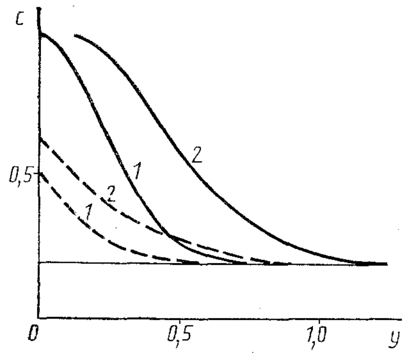

Fig. 3

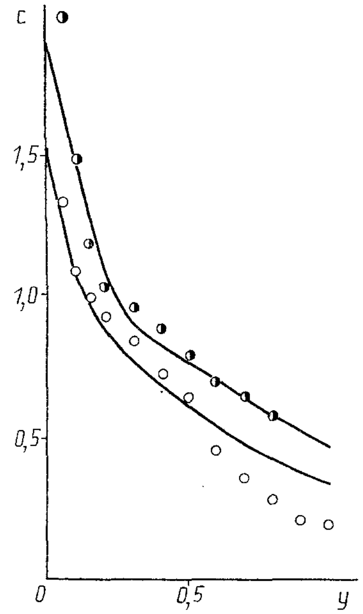

Fig. 4

Fig. 3. Concentration distribution of the impurity across the depth of the diffusion layer (calculation from Eq. (1)); $D = 0.065 \exp(-11{,}100/RT)$ cm^2/sec, $c_0 = 0.2\%$, $c_f = 1.0\%$; 1) $t = 0.5$ h; 2) 1.5 h; dashed curves, $4\pi a^2 n(\lambda D/\lambda a + D) = 0$, $T = 900$°C, $\beta = 10^{-5}$ cm/sec; solid curves, 1) $t_1 = 0.15$ h, $t_2 = 0.35$ h; 2) $t_1 = 0.4$ h, $t_2 = 1.1$ h; $4\pi a^2 n(\lambda_1 D_1/\lambda_1 a + D_1) = 100$ h^{-1}, $T_1 = 800$°C, $\beta_1 = 10^{-3}$ cm/sec, $c_{*1} = 0.2\%$; $4\pi a^2 n(\lambda_2 D_2/\lambda_2 a + D_2) = 50$ h^{-1}, $T_2 = 900$°C, $\beta_2 = 10^{-5}$ cm/sec, $c_{*2} = 5\%$, c, %; y, mm.

Fig. 4. Concentration distribution of carbon in steel on nonisothermal saturation; points mark experimental data, curves denote calculation from Eq. (1)-(3), $c_*(T)$ is an equilibrium value relative to carbides Fe_3C, $4\pi a^2(\lambda D/\lambda a + D) = 0.9$ h^{-1}, $T = 300$-900°C.

emit with another, and the second pertains to the reverse situation. As numerical calculations indicated, this regularity also holds, when the regions with defects containing no impurity are taken into account.

It follows from predictions by the model (1)-(3) for a wide range of $c_*(T)$ and $\lambda(T)$ that the size of the diffusion layer in the thermal cycling saturation of the material with defects is not larger than that obtained in a defect-free material under isothermal conditions at a maximal temperature. This is not the case, however, if consideration is also given to a temperature dependence for the rate of interaction processes of the impurity atoms with the metal surface. In a more general case, at the metal surface we must examine the boundary condition of the third kind

$$-D\left.\frac{\partial c}{\partial y}\right|_{y=0} = \beta(T)\left(c_f - c|_{y=0}\right),$$

where β defines the total rate of all surface processes. Then, as the numerical modeling established, if the thermal activity $c_*(T)$ is an increasing function of temperature (the defects trap the impurity at low temperatures and emit it at high temperatures), the effect of the diffusion layer enlargement manifests itself, when the rate of surface processes decreases with rising temperature. In this case the impurity, emitted from the defects at high temperatures, does not escape through the metal surface, but, by ensuring a high concentration gradient in the matrix, increases the flux deep into and, consequently, the total size of the diffusion layer. Figure 3 exemplifies a distribution of the impurity concentration in the metal during nonisothermal saturation for the above case. The same figure gives, for comparison, the concentration distributions on isothermal saturation at a maximal temperature. We employed a diffusion coefficient for carbon in austenite [2] and a mass transfer coefficient $\beta = 10^{-5}$-10^{-3} cm/sec in computations. In the case when the defects capture the impurity with high temperatures and emit it with low temperatures the effect is exhibited at c_*, which is an increasing function of temperature.

Thus, it is shown that the presence, in the metal, of isolated defects able to entrap the impurity at certain temperatures and to emit it at others can markedly change not only the rate, but also the character of mass transfer from the surface to the solid solution. The relationships, derived in the current study for the nonisothermal mass transfer in the system with isolated traps, can be utilized in devising new technologies of the thermal-cycling chemicothermal treatment of metals.

The main problem lies in adapting the model, i.e., in identifying the traps really affecting the process of nonisothermal saturation of the metal. Its solution is complicated by the fact that fairly complex temperature–time modes are realized in the majority of experiments. Figure 4 compares the experimental data on the concentration distribution of carbon in steel after nonisothermal saturation and the calculations from Eqs. (1)-(3). As the traps, we considered inclusions of carbides Fe_3C, whose size variations were neglected. A temperature dependence of the parameter $4\pi a^2 n \frac{\lambda D}{\lambda a + D}$, characterizing the rate of carbon exchange between the matrix and carbides, was selected from the condition of the best agreement with the experiment. In calculations we used the diffusion coefficient $D = 1.78 \cdot 10^{-7}$ cm^2/sec, determined for nonisothermal conditions in a relevant temperature range [2]. Qualitative and satisfactory quantitative agreement between the theoretical curves and the experimental points is evident.

It should be noted that fairly strong simplifying assumptions and rather general notions as to properties of the traps were employed in deriving the equations. Further on, we suppose to consider the process of nonisothermal diffusion, with allowance for properties of various types of isolated defects, and the effect of extended defects (of grain and dislocation boundaries) on nonisothermal saturation of the metal.

NOTATION

a, radius of the traps; c, c_f, c_i, c_*, concentration of the impurity and its boundary, initial, and equilibrium values; D, diffusion coefficient; L, linear scale of the process; J, dimensionless mass flux; s, dimensionless concentration in the traps; T, temperature; t, y, time and coordinate; α, coefficient of exchange with the traps introduced in Eq. (4); σ, dimensionless concentration of the impurity; τ, η, dimensionless time and coordinate.

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