Mathematical Modelling of Diffusive
and Mechanical Processes in Bodies with Microstructure

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Abstract: The continuum-thermodynamical approach is proposed for describing mechanical and diffusive processes in bodies with microstructure. Different physical states of admixture particles in a local body structure are taken into account. Features of a stressed-deformable state are discussed on an example of diffusive saturation of a layer in this case.
Key words: thermodynamical model, diffusion and mechanics, microstructure

I. INTRODUCTION

A local microscopic structure of real solid bodies significantly influences the process of admixture particle diffusion [1]. These particles are in different physical states when they occupy different positions in a structure of solid solutions, polycrystalline bodies or fine-grained media (for example, in different kinds of interstices of solid solutions or on a boundary and in space of a grain of polycrystalline body, etc.). In these states admixture particles are characterized by distinct concentration *coefficients* and mobilities.

In a macroscopic description of mechanical and diffusion processes in such bodies we can frequently be restricted to consideration of two different states of admixture particles. It is in agreement with different diffusion coefficients. Such a mass transfer process is accompanied by admixture transition from one state into another. In this case mechanical stresses caused by the redistribution of admixture particles depend not only on the gradients of their concentrations, but also on their local distribution between the states.

The continuum approach describing processes of diffusion by two ways was proposed in paper [2]. Certain generalizations and mathematical aspects of the continuum approach applications were considered in works [3-5]. Almost simultaneously a more general continuum-thermo-dynamical approach was formulated in articles [6, 7]. Continuum representations [8] and methods of non-equilibrium thermodynamics [9] were used for modelling constitutive equations. Such investigations are summed up in monograph [10].

Certain generalization of the continuum-thermodynamical approach to the description of mechanical and diffusive processes in bodies with microstructure is presented below, as well as the results of investigating the processes in a layer. A number of non-classical distributions are

quantitatively described for admixture concentration and corresponding contributions of concentrations into stresses. Areas of applicability for approximate models are established, in particular, for the models with effective characteristics.

II. REFERENCE POSITIONS

Let us assume that a body is inserted into the three-dimensional Euclidean space referring to the rectangular Cartesian set of coordinates $\{x_\alpha\}$ with the frame $(O, \vec{i}_\alpha)$, here $\vec{i}_\alpha$ form the orthonormal base $(\alpha = 1, 2, 3)$.

In a macroscopic description a body is considered as a spatially heterogeneous three component thermodynamical system $\mathbf{K}^*$. As a component we take particles of the basic material $\mathbf{K}_0^*$ forming a deformable matrix, and admixture particles in different physical states $\mathbf{K}_1^*$ and $\mathbf{K}_2^*$ (admixture consists of particles of one chemical kind). Continuum K_i $(i = 0, 1, 2)$ is assigned to each component $\mathbf{K}_i^*$ of the body. And the whole body is associated with a continuum of mass centres K_c [11]. Then the processes of deformation and heat transfer are described with the use of kinematic characteristics of continuum K_c. The diffusion processes are treated as motion of points of continuums K_i relative to the points of continuum K_c.

We assume the hypothesis of local thermodynamical equilibrium [11, 12]. The local state of the system is defined by values of conjugate thermodynamical parameters: absolute temperature T and the entropy s; density the components of the Cauchy stress tensor $\sigma^{\alpha\beta}$ and the components of the deformation tensor $\varepsilon_{\alpha\beta}$ $(\alpha, \beta = 1, 2, 3)$; the chemical potentials μ_i' and the mass concentrations of the body components C_i $(C_i = \rho_i / \rho$, where ρ_i is the density of the component i, $\rho = \Sigma \rho_i$ is the total density of the system).

The state parameters define the change of the internal energy density u. Taking into account $\Sigma C_i = 1$, we write the corresponding Gibbs equation in the form [10, 13]

$$du = Tds + \frac{1}{\rho} \sum \sigma^{\alpha\beta} d\varepsilon_{\alpha\beta} + \sum \mu_i dC_i$$
$$(\alpha, \beta = 1, 2, 3; \ i = 1, 2), \tag{1}$$

where $\mu_i = \mu_i' - \mu_0'$ is the relative chemical potential of admixture particles in the state i.

Let us assume now the internal energy density u as a thermodynamical potential, i.e. we suppose the functional dependence $u = u(s, \varepsilon_{\alpha,\beta}, C_i)$ is known. Then from the Gibbs equation (1) we obtain the general form of the state equations

$$T = \frac{\partial u}{\partial s}, \quad \sigma^{\alpha\beta} = \rho \frac{\partial u}{\partial \varepsilon_{\alpha\beta}}, \quad \mu_i = \frac{\partial u}{\partial C_i}$$
$$(\alpha, \beta = 1, 2, 3; \ i = 1, 2). \tag{2}$$

Then the dependences

$$T = T\left(s, \varepsilon_{\alpha\beta}, C_i\right), \quad \sigma^{\alpha\beta} = \sigma^{\alpha\beta}\left(s, \varepsilon_{\alpha\beta}, C_i\right),$$
$$\mu_i = \mu_i\left(s, \varepsilon_{\alpha\beta}, C_i\right) \quad (\alpha, \beta = 1, 2, 3; \ i = 1, 2) \tag{3}$$

that follow from Eqs. (2), are used in a linearized form.

From the laws of conservation of mass, momentum, and energy we obtain [10]

$$\frac{1}{\rho}\frac{d\rho}{d\tau} = -\vec{\nabla} \cdot \vec{v}, \quad \rho \frac{dC_i}{d\tau} + \vec{\nabla} \cdot \vec{J}_i = (-1)^2 J \qquad (i = 1, 2);$$

$$\rho \frac{d\vec{v}}{d\tau} = \vec{\nabla} \cdot \hat{\sigma} - \sum \rho_i \vec{\nabla} \psi_i',$$
$$\rho \frac{ds}{d\tau} = -\vec{\nabla} \cdot \vec{J}_s + \sigma_s, \tag{3}$$

where $\vec{J}_i = \rho_i \left(\vec{v}_i - \vec{v}\right)$ is the diffusion flux, $\vec{v}_i$ is the velocity field of points of the continuum K_i, $\vec{v} = \rho^{-1} \Sigma \rho_i \vec{v}_i$ is the velocity field of points of the mass centre continuum K_c, J is the scalar mass flow (it is concerned with particle transitions between the states), $\hat{\sigma} = \Sigma \sigma_{\alpha\beta} \vec{i}_\alpha \otimes \vec{i}_\beta$ is the Cauchy stress tensor [8], ψ_i' is the conservative $\left(\partial \psi_i'/\delta \tau = 0\right)$ potential $(i = 0, 1, 2)$; $\vec{J}_s = \vec{J}_Q / T$ is the entropy flux, $\sigma_s = \left(JX + \vec{J}_Q \cdot \vec{X}_Q + \Sigma \vec{J}_i \cdot \vec{X}_i\right)/T \geq 0$ is the entropy production, $X = \mu_2 - \mu_1$ is the thermodynamical force conjugated to the flow J, $\vec{X}_Q = -\vec{\nabla} T / T$ is the thermodynamical force conjugated to the heat flux $\vec{J}_Q$, $\vec{X}_i = -\vec{\nabla}\left(\mu_i + \psi_i\right)$ is the thermodynamical force conjugated to the flux $\vec{J}_i \left(\psi_i = \psi_i' - \psi_0', i = 1, 2\right)$; $d/d\tau = \partial/\partial \tau + \vec{v} \cdot \vec{\nabla}$ is the operator of material derivative, $\vec{\nabla}$ is the nabla-operator, τ is time. The symbol $\otimes$ and the dot between quantities denote tensor and scalar multiplication.

Here we have allowed for the normalization of both diffusion flux $\Sigma \vec{J}_i = 0$ and concentrations $\Sigma C_i = 1$. We also neglect viscosity effects.

The thermodynamical fluxes and forces define the change of density of the kinetic potential Φ that is a part of the internal body energy related to non-equilibrium processes, i.e. [11, 14]

$$d\Phi = JdX + \vec{J}_Q \cdot d\vec{X}_Q + \sum \vec{J}_i \cdot d\vec{X}_i. \tag{5}$$

If $\Phi = \Phi\left(X, \vec{X}_Q, \vec{X}_1, \vec{X}_2\right)$, then we define the thermodynamical fluxes by the formulae

$$J = \frac{d\Phi}{dX}, \quad \vec{J}_Q = \frac{d\Phi}{d\vec{X}_Q}, \quad \vec{J}_i = \frac{d\Phi}{d\vec{X}_i}, \quad (i = 1, 2) \qquad (6)$$

where $\partial\Phi/\partial\vec{X} \equiv \Sigma\vec{i}_\alpha\,\partial\Phi/\partial X_\alpha$ is the gradient of the scalar field Φ, X_α are the components of the vector $\vec{X}$ in the chosen Cartesian set of coordinates.

In this case, for an isotropic body basing on the Curie principle [11] the relations between fluxes and forces obtained from Eqs. (6), are

$$J = J(X), \quad \vec{J}_Q = \vec{J}_Q\left(\vec{X}_Q, \vec{X}_1, \vec{X}_2\right), \quad \vec{J}_i = \vec{J}_i\left(\vec{X}_Q, \vec{X}_1, \vec{X}_2\right).$$

In models of solid mechanics, the kinetic equations are mostly used in the linear forms, as follows

$$J = \lambda X, \quad \vec{J}_Q = \hat{L}_{QQ} \cdot \vec{X}_Q + \sum \hat{L}_{Qi} \cdot \vec{X}_i,$$
$$\vec{J}_i = \hat{L}_{iQ} \cdot \vec{X}_Q + \sum \hat{L}_{ij} \cdot \vec{X}_j, \qquad (7)$$

where λ and $\hat{L}_{QQ}, \hat{L}_{Qi}, \hat{L}_{iQ}, \hat{L}_{ij}\ (i, j = 1, 2)$ are scalar and tensor kinetic coefficients. In a general case these coefficients can be functions of the intensive variables of the state.

On the basis of the relationships (1)-(7), taking into account kinematic dependences, we can construct a complete set of equations of the model for the description of the coupled mechanical, heat transfer and diffusion processes. In many cases such a set of equations is written with the use of kinematic characteristics of the mass centre continuum.

III. THE MODEL OF MECHANICAL AND HETERODIFFUSION PROCESSES

Let us specify the above-mentioned set of equations (1)-(7) for isothermal conditions and small deformations. We do not make a difference between contravariant and covariant quantities for small deformations. Then we define a local thermodynamical state by the values of parameters $\rho^{-1}\sigma_{\alpha\beta} - \varepsilon_{\alpha\beta}$, $\mu_i - C_i$, where

$$\varepsilon_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha}\right) \qquad (8)$$

are the components of the deformation tensor [8], u_α are the components of the vector of displacements $\vec{u}$, and x_a are the Cartesian coordinates of the mass centre continuum $(\alpha, \beta = 1, 2, 3; i = 1, 2)$.

Let us choose a state corresponding to the state of an unlimited body in the absence of an external action as a reference one. In this state $\sigma_{\alpha\beta} = 0$, $\varepsilon_{\alpha\beta} = 0$; $\mu_i = \mu_i^0$, $C_i = C_i^0$.

If we assume the displacement vector $\vec{u}$ and the concentrations of the *admixtures in form* $c_i = C_i - C_i^0$ $(i = 1, 2)$ as resolving functions, then in the linear approximations of (2) we can write in the form [10]

$$\sigma_{\alpha\beta} = \left[\left(K - \frac{2}{3}G\right)\varepsilon - K\sum\beta_i c_i\right]\delta_{\alpha\beta} + 2G\varepsilon_{\alpha\beta},$$
$$\mu_i = \mu_i^0 - \frac{K}{\rho_0}\beta_i\varepsilon + \sum_j \bar{d}_{ij}c_j, \qquad (9)$$

where K is the compression modulus, G is the modulus of shear; β_i are the concentration coefficients; $\bar{d}_{ij}$ are the coefficients of the dependence of chemical potentials on concentrations; $\varepsilon = \varepsilon_{\alpha\alpha}$ is the first invariant of the deformation tensor (we assume summation over pairs of the same Greek indices), and $\delta_{\alpha\beta}$ is the Kronecker symbol.

If we neglect the convective components $(\vec{v} \cdot \vec{\nabla}c_i \cong 0, \vec{v} \cdot \vec{\nabla} \otimes \vec{v} \cong 0)$, the internal (mass) forces $(\rho\partial\vec{v}/\partial\tau \cong 0)$ and the external mass forces, then the balance equations for concentrations and momentum take the form

$$\rho_0\frac{\partial c_i}{\partial\tau} = -\vec{\nabla}\cdot\vec{J}_i + (-1)^i J \quad (i = 1, 2);$$
$$\vec{\nabla}\cdot\vec{\sigma} = 0 \quad \left(\vec{\nabla}\times\vec{\nabla}\times\hat{\varepsilon} = 0\right), \qquad (10)$$

where $\hat{\varepsilon} = \varepsilon_{\alpha\beta}\vec{i}_\alpha \otimes \vec{i}_\beta$ is the *deformation tensor* $(\alpha, \beta = 1, 2, 3)$.

According to the kinetic equation (7), fluxes $\vec{J}_i$ are proportional to the gradients of chemical potentials, and scalar flow J is proportional to its local rate. Hence, for the linear state equations (9) we can write

$$\vec{J}_1 = -\rho_0\left(\bar{D}_1\vec{\nabla}c_1 + \bar{D}_3\vec{\nabla}c_2 - \bar{D}_1^\varepsilon\vec{\nabla}\varepsilon\right),$$
$$\vec{J}_2 = -\rho_0\left(\bar{D}_4\vec{\nabla}c_1 + \bar{D}_2\vec{\nabla}c_2 - \bar{D}_2^\varepsilon\vec{\nabla}\varepsilon\right), \qquad (11)$$
$$J = -\rho_0\left(\bar{k}_1 c_1 - \bar{k}_2 c_2 - \bar{k}_\varepsilon\varepsilon\right),$$

where $\bar{D}_l$ are the diffusion coefficients $(l = 1, ..., 4)$ $\bar{D}_i^\varepsilon$ is the coefficient of the influence of volumetric deformation field gradient on mass fluxes $(i = 1, 2)$; $\bar{k}_i$ are the kinetic coefficients for the process of local particle intertransitions from one state into another, and $\bar{k}_\varepsilon$ is the coefficient defining the influence of volumetric deformation field on this process.

Let us substitute (8), (9) and (11) into (10) and take the constant coefficients (material characteristics) in the state equations (8) and the kinetic model relationships (11). Then we obtain the set of equations for heterodiffusion, in the form

$$\frac{\partial c_1}{\partial \tau} = \bar{D}_1 \Delta c_1 + \bar{D}_3 \Delta c_2 - \bar{D}_1^\varepsilon \Delta \varepsilon - \bar{k}_1 c_1 + \bar{k}_2 c_2 + \bar{k}_\varepsilon \varepsilon,$$

$$\frac{\partial c_2}{\partial \tau} = \bar{D}_4 \Delta c_1 + \bar{D}_2 \Delta c_2 - \bar{D}_2^\varepsilon \Delta \varepsilon + \bar{k}_1 c_1 - \bar{k}_2 c_2 - \bar{k}_\varepsilon \varepsilon;$$

$$G \Delta \vec{u} + \left(K + \frac{G}{3} \right) \vec{\nabla} \vec{\nabla} \cdot \vec{u} - K \sum \beta_i \vec{\nabla} c_i = 0. \qquad (12)$$

Here $\Delta = \vec{\nabla} \cdot \vec{\nabla}$ is the Laplace operator.

IV. MECHANICAL AND HETERODIFFUSION PROCESSES IN A LAYER

Let us consider a layer of thickness l referred to Cartesian coordinates, i.e. X-axis is normal to its surfaces and the origin of the coordinate set lies on the upper surface. The concentration distributions are known in the initial time $\tau = 0$ in the layer space $0 \le x \le l$ and the chemical potentials of admixture particles are given on the layer boundaries $x = 0, l$, i.e.

$$c_i(x, 0) = c_i^0(x), \quad \mu_i(0, \tau) = \mu_i^\Sigma(\tau),$$

$$\mu_i(l, r) = \mu_i^{\Sigma \times}(\tau) \quad (i = 1, 2). \qquad (13)$$

The layer boundaries are free against the external mechanical action $\sigma_{xx}(0, \tau) = \sigma_{xx}(l, \tau) = 0$. Let us assume that the layer edges are immovable on infinities $(y, z \to \pm\infty)$, so $\varepsilon_{yy}(x, \tau) = \varepsilon_{xx}(x, \tau) = 0$. The tensor components of deformation ε_{xx} and stress σ_{yy} and σ_{zz} are nonzero only. From the equilibrium conditions $\vec{\nabla} \cdot \hat{\sigma} = 0$ and the condition $\sigma_{xx}(0, \tau) = \sigma_{xx}(l, \tau) = 0$ on the layer boundaries we also have $\sigma_{xx}(x, \tau) = 0$ $(0 \le x \le l)$. From this equality and the state equation (9) we find for the components ε_{xx}

$$\varepsilon_{xx} = \beta_1^0 c_1 + \beta_2^0 c_2, \qquad (14)$$

where $\beta_i^0 = \xi \beta_i$, $\xi = 3K (3K + 4G)^{-1}$, $i - 1, 2$.

Let us substitute (14) into (12) and (9). Then, to determine the concentrations of admixture particles we obtain the following set of differential equations

$$\frac{\partial c_1}{\partial \tau} = D_1 \frac{\partial^2 c_1}{\partial x^2} + D_3 \frac{\partial^2 c_2}{\partial x^2} - k_1 c_1 + k_2 c_2,$$

$$\frac{\partial c_1}{\partial \tau} = D_4 \frac{\partial^2 c_1}{\partial x^2} + D_2 \frac{\partial^2 c_2}{\partial x^2} + k_1 c_1 - k_2 c_2, \qquad (15)$$

and stresses and chemical potentials are found from the algebraic equations

$$\sigma_{yy} = \sigma_{zz} = -2G \left(\beta_1^0 c_1 + \beta_2^0 c_2 \right), \quad \mu_i = \mu_i^0 + \sum_j d_{ij} c_j,$$

$$i, j = 1, 2, \qquad (16)$$

where

$$d_{ij} = \bar{d}_{ij} - \beta_i^0 \beta_j \rho_0^{-1} K, \quad k_j = \bar{k}_j - \beta_j^0 \bar{k}_\varepsilon \quad (i, j = 1, 2);$$

$$D_1 = \bar{D}_1 - \beta_1^0 \bar{D}_1^\varepsilon, \quad D_3 = \bar{D}_3 - \beta_2^0 \bar{D}_1^\varepsilon,$$

$$D_4 = \bar{D}_4 - \beta_1^0 \bar{D}_2^\varepsilon, \quad D_2 = \bar{D}_2 - \beta_2^0 \bar{D}_2^\varepsilon$$

are the corrected characteristics of the layer material.

Taking into account the relationships (16) for the chemical potentials, we write the boundary conditions (13) for the concentrations, namely

$$c_i(0, \tau) = c_i^\Sigma(\tau), \quad c_i(l, \tau) = c_i^{\Sigma \times}(\tau), \qquad (17)$$

where $c_i^\Sigma, c_i^{\Sigma \times}$ $(i = 1, 2)$ are the time-functions defined by the values of the chemical potentials μ_i^Σ and $\mu_i^{\Sigma \times}$, namely

$$c_1^\Sigma(\tau) = \bar{a}^{-1} \left(\mu_1^\Sigma d_{22} - \mu_2^\Sigma d_{12} \right), \quad c_1^{\Sigma \times}(\tau) = \bar{a}^{-1} \left(\mu_1^\Sigma d_{22} - \mu_2^{\Sigma \times} d_{12} \right);$$

$$c_2^\Sigma(\tau) = \bar{a}^{-1} \left(\mu_2^\Sigma d_{11} - \mu_1^\Sigma d_{21} \right), \quad c_2^{\Sigma \times}(\tau) = \bar{a}^{-1} \left(\mu_2^\Sigma d_{11} - \mu_1^{\Sigma \times} d_{21} \right);$$

$$\bar{\mu}_i^\Sigma = \mu_i^\Sigma - \mu_i^0, \quad \bar{\mu}_i^{\Sigma \times} = \mu_i^{\Sigma \times} - \mu_i^0, \quad \bar{a} = d_{11} d_{21} - d_{12} d_{21}.$$

Similarly, the problem is reduced to determine the concentrations $c_i(x, \tau)$ from (15) using the boundary conditions (17) and the initial ones (13). When functions $c_i(x, \tau)$ have been found, the stresses are determined by the formula (16). In this case total diffusion flow J_x and the total mass of admixture $m(\tau)$ passing across the layer surface $x = l$ through time-interval $\tau \in [0; \tau]$, are defined as follows

$$J_x(l, \tau) = -\rho_0 \left(D^{(1)} \frac{\partial c_1}{\partial x} + D^{(2)} \frac{\partial c_2}{\partial x} \right) \Bigg|_{x = l},$$

$$m(\tau) \equiv \int_0^\tau J_x(l, \tau) d\tau, \qquad (18)$$

where $D^{(1)} = D_1 + D_4$ and $D^{(2)} = D_2 + D_3$.

To construct a solution of the original problem (13), (17) and (15), we apply the finite Fourier sine transformation over a space coordinate and the Laplace integral transformation with respect to time. The solution is as follows

$$f_i(x, \tau) = c_i(x, \tau) - c_i^\Sigma(\tau) \left(1 - \frac{x}{l} \right) - c_i^{\Sigma \times}(\tau) \frac{x}{l}, \qquad (19)$$

which satisfies the initial and the boundary conditions

$$f_i(x,0) = c_i^0 - c_i^\Sigma(0)\left(1-\frac{x}{l}\right) - c_i^{\Sigma\times}(0)\frac{x}{l};$$

$$f_i(0,\tau) = f_i(l,r) = 0, \quad i = 1,2, \tag{20}$$

where

$$c^\Sigma(\tau) = k_1 c_1^\Sigma(\tau) - k_2 c_2^\Sigma(\tau),$$

$$c^{\Sigma\times}(\tau) = k_1 c_1^{\Sigma\times}(\tau) - k_2 c_2^{\Sigma\times}(\tau)$$

are the known time-functions.

We find the corresponding set of equations for functions $f_i(x,\tau)$ from the original set of Eqs. (15) using the expressions (19). In the case of zero boundary conditions (20) we find its solution in the form of Fourier's series

$$f_i(x,\tau) = \sum_{n=1}^{\infty} f_i^{(n)}(\tau) \sin \pi_n x, \tag{21}$$

where $\pi_n = n\pi/l$ $(n = 0,1,2...)$. Then the set of ordinary differential equations for expansion coefficients $f_i^{(n)}(\tau)$ $(i = 1, 2; n = 1, 2, ...)$ with the following initial conditions

$$f_i^{(n)}(0) = c_{i(n)}^0 - \frac{2}{\pi_n l} c_i^\Sigma(0) + \frac{2(-1)^n}{\pi_n l} c_i^{\Sigma\times}(0) \tag{22}$$

is solved by the Laplace transformation.

Finally, we find an analytical solution for concentrations in the form of a trigonometric series. Whereas the obtained solution is awkward, we show its explicit form for the following particular case of the initial and boundary conditions

$$c_i(x,0) = 0 \quad (0 \le x \le l); \quad c_i^\Sigma(\tau) = \eta c_0^\Sigma,$$

$$c_2^\Sigma(\tau) = (1-\eta)c_0^\Sigma, \quad c_i^{\Sigma\times}(\tau) = 0, \quad i = 1,2, \tag{23}$$

where c_0^Σ is the constant value of admixture total concentration at the layer surface, and η is the nonnegative parameter satisfying the inequality $1 \ge \eta \ge 0$.

Then for concentrations $c_i(x,\tau)$ $(i = 1,2)$ and their sum $c(x,t)$ we obtain

$$c_1(x,\tau) = \eta c_0^\Sigma\left(1-\frac{x}{l}\right) - \frac{k_* c_0^\Sigma D^{(2)}}{a}\left[1-\frac{x}{l} - \frac{\sinh\eta_0(1-x/l)}{\sinh\eta_0}\right] +$$

$$- \frac{2c_0^\Sigma}{l}\left[R_{11}(x,\tau) - R_{12}(x,\tau)\right], \tag{24}$$

$$c_2(x,\tau) = (1-\eta)c_0^\Sigma\left(1-\frac{x}{l}\right) + \frac{k_* c_0^\Sigma D^{(1)}}{a}\left[1-\frac{x}{l} - \frac{\sinh\eta_0(1-x/l)}{\sinh\eta_0}\right] +$$

$$+ \frac{2c_0^\Sigma}{l}\left[R_{21}(x,\tau) - R_{22}(x,\tau)\right], \tag{25}$$

$$c(x,\tau) = c^\Sigma\left(1-\frac{x}{l}\right) + \frac{k_* c^\Sigma D^{(0)}}{a}\left[1-\frac{x}{l} - \frac{\sinh\eta_0(1-x/l)}{\sinh\eta_0}\right] +$$

$$+ \frac{2c^\Sigma}{l}\left[R_{c1}(x,\tau) - R_{c2}(x,\tau)\right], \tag{26}$$

where

$$k_* = \eta k_1 - (1-\eta)k_2, \quad \eta_0 = l(a/b)^{1/2},$$

$$a = k_1 D^{(2)} + k_2 D^{(1)},$$

$$b = D_1 D_2 - D_3 D_4$$

are the coefficients defining an asymptotic behaviour of the solution;

$$R_{11}(x,\tau) = \sum_{n=1}^{\infty} \sin(\pi_n x) R_n^{(21)} e^{s_n^{(1)}\tau},$$

$$R_{12}(x,\tau) = \sum_{n=1}^{\infty} \sin(\pi_n x) R_n^{(22)} e^{s_n^{(2)}\tau},$$

$$R_{21}(x,\tau) = \sum_{n=1}^{\infty} \sin(\pi_n x) R_n^{(11)} e^{s_n^{(1)}\tau},$$

$$R_{22}(x,\tau) = \sum_{n=1}^{\infty} \sin(\pi_n x) R_n^{(12)} e^{s_n^{(2)}\tau},$$

$$R_{c1}(x,\tau) = \sum_{n=1}^{\infty} \sin(\pi_n x) R_n^{(c1)} e^{s_n^{(1)}\tau},$$

$$R_{c2}(x,\tau) = \sum_{n=1}^{\infty} \sin(\pi_n x) R_n^{(c2)} e^{s_n^{(2)}\tau},$$

are monotonously decreasing in time functions;

$$R_n^{(21)} = \eta \bar{s}_n^1 + D_n^{(2)\eta} + \frac{k_* \pi_n^2 D^{(2)}}{s_n^{(1)}},$$

$$R_n^{(22)} = \eta \bar{s}_n^2 + D_n^{(2)\eta} + \frac{k_* \pi_n^2 D^{(2)}}{s_n^{(2)}}$$

$$R_n^{(11)} = -(1-\eta)\bar{s}_n^1 + D_n^{(1)\eta} + \frac{k_* \pi_n^2 D^{(1)}}{s_n^{(1)}},$$

$$R_n^{(12)} = -(1-\eta)\bar{s}_n^2 + D_n^{(1)\eta} + \frac{k_* \pi_n^2 D^{(1)}}{s_n^{(2)}},$$

$$R_n^{(c1)} = R_n^{(11)} - R_n^{(21)}, \quad R_n^{(c2)} = R_n^{(12)} - R_n^{(22)};$$

$$D_n^{(1)\eta} = \pi_n^2\left[\eta D_4 - (1-\eta)D_1\right],$$

$$D_n^{(2)\eta} = \pi_n^2 \left[\eta D_2 - (1-\eta) D_3 \right],$$

$$\overline{s}_n^{(i)} = k + s_n^{(i)} \quad (i=1,2),$$

$$\overline{s}_n^{(i)} = k + s_n^{(i)} \quad (i=1,2),$$

$$s_n^{(1,2)} = -\frac{1}{2} \delta_n^{(1)} \pm \left(\frac{1}{4} \delta_n^{(1)^2} - \pi_n^2 \delta_n^{(2)} \right)^{1/2},$$

$$\delta_n^{(1)} = k + \pi_n^2 D, \quad \delta_n^{(2)} = a + \pi_n^2 b,$$

$$k = k_1 + k_2, \quad D = D_1 + D_2.$$

Let us substitute the obtained relationships (24) and (25) into (18). Then the expression of the total mass flow across the layer is written in the form

$$J_l(l,\tau) = \frac{\rho c_0^{\Sigma} D^{\eta}}{l} + \frac{2\rho c_0^{\Sigma}}{l} \left[R_{p1}(l,\tau) - R_{p2}(l,\tau) \right]. \quad (27)$$

Here

$$R_{p1}(\tau) = \sum_{n=1}^{\infty} (-1)^n \pi_n \overline{s}_n^* \left(D^{\eta} \overline{s}_n^{(1)} + b\pi_n^2 \right) \exp\left\{ s_n^{(1)} \tau \right\},$$

$$R_{p2}(\tau) = \sum_{n=1}^{\infty} (-1)^n \pi_n \overline{s}_n^* \left(D^{\eta} \overline{s}_n^{(2)} + b\pi_n^2 \right) \exp\left\{ s_n^{(2)} \tau \right\},$$

are monotonously decreasing in time functions;

$$\overline{s}_n^* = \left[\pi_n \left(s_n^{(1)} - s_n^{(2)} \right) \right]^{-1}, \quad D^{\eta} = \eta D^{(1)} + (1-\eta) D^{(2)}.$$

If we substitute the expressions (24) and (25) for concentrations $c_i(x,\tau)$ $(i=1,2)$ in the formula (16), then we have for stress the relation

$$\sigma_{yy} = -2G\xi^0 c^{\Sigma} \left\{ \beta^{\eta} \left(1 - \frac{x}{l} \right) + \right.$$

$$+ \frac{k_* D^{\beta}}{a} \left[1 - \frac{x}{l} - \frac{\sinh \eta_0 (1-x/l)}{\sinh \eta_0} \right] + \quad (28)$$

$$\left. - \frac{2}{l} \sum_{n=1}^{\infty} \sin(\pi_n x) \left[R_n^{(\sigma 1)} e^{s_n^{(1)} \tau} - R_n^{(\sigma 2)} e^{s_n^{(2)} \tau} \right] \right\},$$

where

$$R_n^{(\sigma 1)} = \overline{s}_n^* \left[\beta^{\eta} \overline{s}_n^{(1)} + \tilde{D}_n^{\beta} - \frac{k_* \tilde{D}_n^{\beta}}{s_n^{(1)}} \right],$$

$$R_n^{(\sigma 2)} = \overline{s}_n^* \left[\beta^{\eta} \overline{s}_n^{(2)} + \tilde{D}_n^{\beta} - \frac{k_* \tilde{D}_n^{\beta}}{s_n^{(2)}} \right];$$

$$\beta^{\eta} = \eta \beta_1 + (1-\eta) \beta_2, \quad D^{\beta} = \beta_2 D^{(1)} - \beta_1 D^{(2)},$$

$$D_n^{\beta} = \pi_n^2 D^{\beta}, \quad \tilde{D}_n^{\beta} = \beta_1 D_n^{(2)\eta} - \beta_2 D_n^{(1)\eta}.$$

V. INSTANTANEOUS CHANGES OF A LOCAL PARTICLE STATE (EFFECTIVE CHARACTERISTICS)

Let us regard that the relaxation time for diffusion is larger than the relaxation time for the processes of particle transitions from state 1 into state 2 and vice versa, i.e. the local equilibrium distribution of admixture particles between states 1 and 2 in the process of their spatial redistribution is ascertained almost instantaneously. Then, within the time scale, with the condition of the equality of the chemical potentials, we obtain that

$$\mu_2(x,\tau) = \mu_1(x,\tau) \qquad (0 \le x \le l) \quad (29)$$

for any moment τ.

Notice that in this case $J \ne 0$, but its value is not already defined by the expression (11).

The expressions (16) for the chemical potentials are substituted into the equilibrium condition (29). Then from the obtained relationships we define concentrations $c_1(x,\tau)$, $c_2(x,\tau)$ in terms of the sum of concentrations

$$c(x,\tau) = c_1(x,\tau) + c_2(x,\tau).$$

So we have

$$c_1(x,\tau) = \frac{k_2}{k} c(x,\tau),$$

$$c_2(x,\tau) = \frac{k_1}{k} c(x,\tau), \quad (30)$$

where $k = k_1 + k_2$. Adding the equations (15) for the diffusion, we obtain

$$\frac{\partial c}{\partial \tau} = D^{(1)} \frac{\partial^2 c_1}{\partial x^2} + D^{(2)} \frac{\partial^2 c_2}{\partial x^2}, \quad (31)$$

where

$$D^{(1)} = D_1 + D_4, \quad D^{(2)} = D_2 + D_3.$$

Under these conditions concentration $c(x,\tau)$ is named an effective concentration, i.e $c(x,\tau) \equiv c_{ef}(x,\tau)$.

Substituting (30) into (16) and (31) for finding effective stresses and concentrations we obtain

$$\sigma_{yy} = \sigma_{zz} = -2G\xi \beta_{ef} c_{ef},$$

$$\frac{\partial c_{ef}}{\partial \tau} = D_{ef} \frac{\partial^2 c_{ef}}{\partial x^2}. \quad (32)$$

Here

$$\beta_{ef} = k^{-1}\left(\beta_1 k_2 + \beta_2 k_1\right),$$

$$D_{ef} = k^{-1}\left(k_1 D^{(2)} + k_2 D^{(1)}\right) \tag{33}$$

are the effective coefficients of concentration related to both volume and diffusion changes.

Under the conditions of thermodynamical equilibrium relative to particle transition on the layer surface for finding the solutions of the initial-boundary value problem, we need to substitute coefficient η by k_2/k and $1-\eta$ by k_1/k in the formulae for the concentrations, total flow and stresses. Then the coefficient k_* is to be assumed zero, i.e. $k_* = 0$.

VI. RESULTS OF NUMERICAL ANALYSIS

Let us show the results of numerical analysis for the concentrations and stresses σ_{yy} on the basis of the solutions (24)-(26) and (28). The estimation of the corresponding model coefficients was taken for isotropic polycristalline bodies assuming the states of admixture particles on a boundary ($i = 1$) and in space ($i = 2$) of a grain as physically different ones. The majority of the source data have been taken from [1].

In calculations we take up $K = 10^{11}$ N/m^2, $G = 4 \cdot 10^{10}$ N/m^2, $\beta_1 = 5 \cdot 10^{-3}$, $\beta_2 = 5 \cdot 10^{-2}$, $D_3 = D_4 = 0$, $l = 10^{-3}$ m. In this case we use the following dimensionless variables $\tau^* = k_2\tau$, $\xi = (k_2/D_1)^{1/2} x$, and also the magnitudes $d = D_2/D_1$ and $q = k_1/k_2$ (the Henry constant).

Remark that parameter η depends on the conditions of mass exchange with an external medium and the medium of subsurface layer. For example, in the case of polycrystalline bodies from a gas medium or liquid one, we can take this parameter as proportional to the ratio of grain boundary area and full interface area. It is possible to propose other variants of interpretation, for example, when the equilibrium distribution of admixture particles between states 1 and 2 is on the interface, then the parameter value is $\eta_2 = k_2/k$.

Typical dependences of the total concentration and stress on the surface distribution of admixture particles between quick and slow ways of diffusion (the value of parameter η) are presented in Figs. 1 and 2.

Figures 3 and 4 show characteristic time-dependences of the total admixture concentration and stresses.
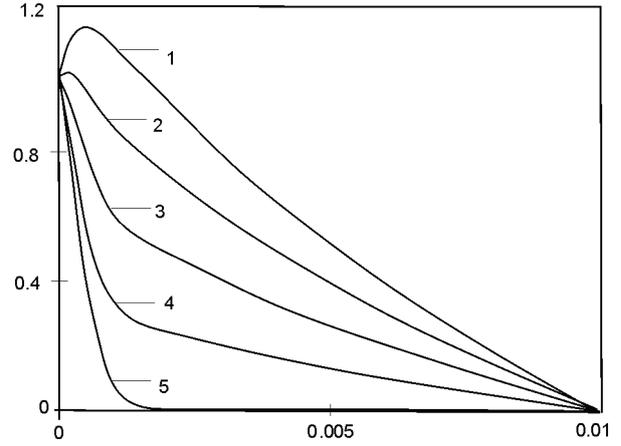
Fig. 1. Distributions of total admixture concentration in a layer for $q = 2 \cdot 10^1$, $d = 5 \cdot 10^{-3}$, $\tau^* = 1,5 \cdot 10^{-2}$; curve 1 for $\eta = 1$, $2 - \eta = 0,75$ $3 - \eta = 0,5$, $4 - \eta = 0,25$, $5 - \eta = 0$
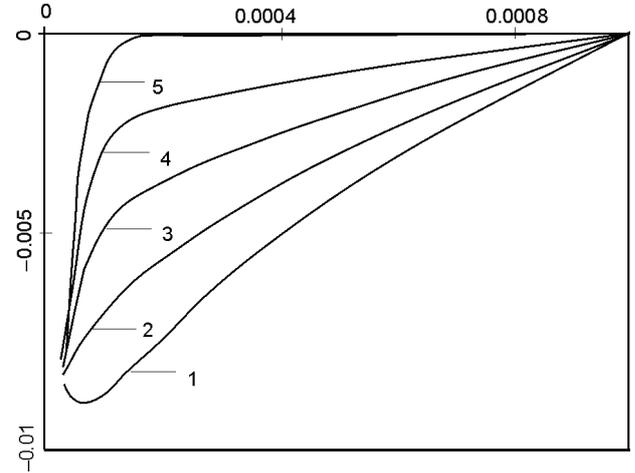
Fig. 2. Distributions of concentrating stresses in a layer for $q = 2 \cdot 10^1$, $d = 5 \cdot 10^{-3}$, $\tau^* = 1,5 \cdot 10^{-2}$; curve 1 for $\eta = 1$, $2 - \eta = 0,75$ $3 - \eta = 0,5$, $4 - \eta = 0,25$, $5 - \eta = 0$
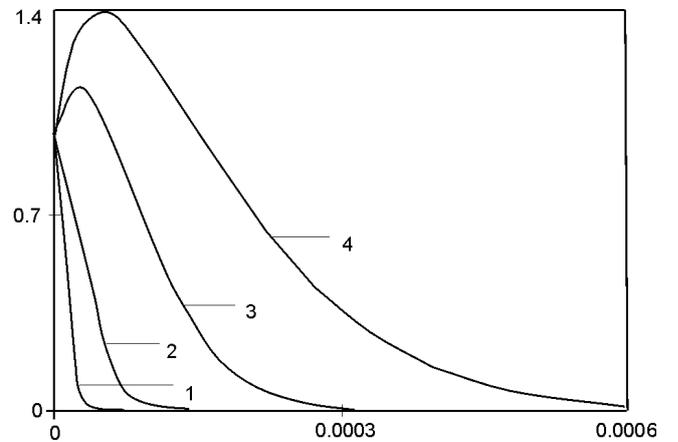
Fig. 3. Behaviour of total admixture concentration distributions in time for $\eta = 1$, $q = 2 \cdot 10^2$, $d = 5 \cdot 10^{-1}$; curve 1 for $\tau^* = 5 \cdot 10^{-4}$, $2 - \tau^* = 5 \cdot 10^{-3}$, $3 - \tau^* = 5 \cdot 10^{-2}$, $4 - \tau^* = 5 \cdot 10^{-1}$
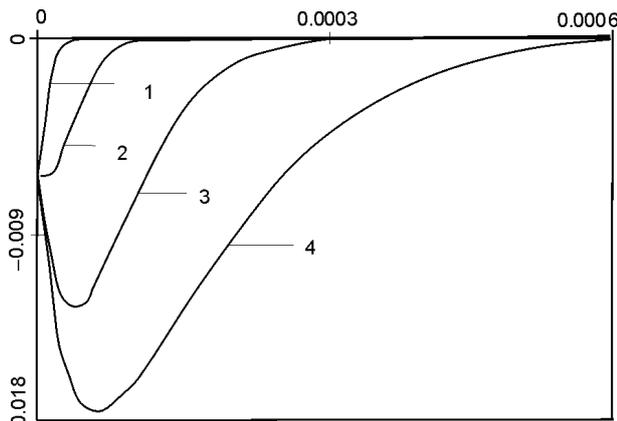
Fig. 4. Behaviour of concentrating stress distributions in time for
$\eta = 1$, $q = 2 \cdot 10^2$, $d = 5 \cdot 10^{-1}$; curve 1 for $\tau^* = 5 \cdot 10^{-4}$, $2 - \tau^* = 5 \cdot 10^{-3}$, $3 - \tau^* = 5 \cdot 10^{-2}$, $4 - \tau^* = 5 \cdot 10^{-1}$

We lay off the function c/c_0^Σ in Figs. 1 and 3 and the quantity in $\sigma_{\alpha\alpha}\left(G_{c_0}^\Sigma\right)^{-1}$ in Figs. 2 and 4 as ordinates. Here the space coordinate x is laid off as abscissa.

Moreover, we have carried out numerical investigation for the dependence of distributions of both the total admixture concentration and stresses on the Henry constant q and the ratio of diffusion coefficients d. Their qualitative behaviour (with some quantitative distinctions) is in accordance with the distributions shown in Figs. 1-4 for the considered interval of parameter values and $q > 1$ and $d < 1$.

VIII. CONCLUSION

From the above-mentioned results, including numerical calculations, it is clear that the distributions of the stresses and concentrations can differ quantitatively and qualitatively from analogous ones related to forbidden inter-transitions of admixture particles between different states (the model of noninteractive flows: $k_1 = k_2 = 0$. The limiting case of instantaneous establishment of local thermodynamical equilibrium between states 1 and 2 (using the effective characteristics on the basis of equations (32) and (33)) is not in agreement with the obtained results, either.

So, in particular, if $\eta \neq k_2/k$, then at $\tau \to \infty$ the obtained concentration distributions are substantially non-linear because $R_{ij}(x,\tau) \to 0$ and $R_{cj}(x,\tau) \to 0$ $(i = 1, 2)$. We ascertain that for small time intervals and in an area near the surface $x = l$, where admixture particle diffusion in state 1 is determined, the values of admixture concentrations and corresponding stresses can be determined with satisfactory accuracy by the use of effective material characteristics.

Notice also that for small values of kinetic coefficients k_i $(i = 1, 2)$ $(q < 2 \cdot 10^2$, $k_2 \square k_1)$ and the near initial time moments and under the same ratio of diffusion coefficients D_1 and D_2, the distributions of stresses and concentrations are in good agreement with the distributions found from the model of noninteractive diffusion flows. With the increase of coefficients k_i $(k_1, k_2 < 1; i = 1, 2)$ the model of non-interactive flows becomes inapplicable. In such cases the obtained solutions are closer to the distributions found with the use of the effective characteristics or the body model, where admixture particles occupy only one position in a physically small element which is related to state 2. Qualitative distinctions in distributions of stresses and concentrations become negligible at decreasing the ratio of kinetic coefficients k_1 and k_2 (Henry equilibrium constant q) and the fixed coefficient $d \geq 10^2$.

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