

Irreversible Mass Transfer during Interaction of Charged Particle Beams with Surface ¹

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Abstract – The equations are suggested for mass fluxes in multi-component media, reflecting the influence of activation parameter on the diffusion coefficients and on other transfer coefficients in irreversible conditions of surface treatment by high energy sources.

The various approximations typical for the solid-phase diffusion are examined. The generalization of thermodynamic approach for the description of irreversible diffusion in chemical compounds is given on the base of conceptions of tensor concentrations and tensor chemical potentials.

1. Introduction

In term of modern irreversible thermodynamics, the deformable media behavior ones describe with the help of so called additional parameters, the introduction way of which in the medium model could be different. Additional parameter reflects the switching-in of the additional degrees of freedom in the formation of system state; bring their part in the heat capacity, in the values of the elastic modulus, the heat expansion coefficient and other physical and mechanical properties determining by the second derivatives of thermodynamic potentials. Particularly, inelastic behavior of materials connects with the existence of internal parameters [1–3], reversible value of which is determined by the level of stresses and strains in the specimen. Detailed analysis shows that the presence and evolution of additional parameters are principal to so irreversible processes as the diffusion (or, in the general case, – mass transfer), especially when they occur under irreversible conditions typical for modern methods of surface treatment by charged beams.

The new physical parameter characterizing the deviation of the system from thermodynamic equilibrium state was suggested and grounded in [4]. The connection of new parameter with the basic thermodynamic variables was shown. The activation parameter (parameter of irreversible state) determining by the deviation of the atom volume from equilibrium value is assumed as the additional parameter

characterizing the deviation degree of the system from equilibrium state. In turn, it was shown in [5], that the atom volume can be regarded as thermodynamic variable when phase diagrams have been constructed. With the help of this parameter the diffusion acceleration is explained in activated layer during surface electron- and ion-beam treatment of the materials. The surface activation leads to the necessity of special description of the new parameter evolution when the system deviates from the equilibrium state in each physical situation. In the first approximation, this process could be described on the base of thermodynamic relaxation theory, the mathematical apparatus of which is very well developed.

2. General correlations

Let V_0 is the volume related to one atom (molecule) in equilibrium state; and V'_0 is the volume related to one atom (molecule) in irreversible (activated) state. Than

$$\eta = \frac{V - V_0}{V'_0 - V_0} \quad (1)$$

– is the parameter (the degree) of the activation. In the equilibrium state we have $V=V_0$ and $\eta=0$. Near by the vicinity of equilibrium state we have $\eta \ll 1$, and $\eta=1$ is typical for full irreversible state ($V=V'_0$).

When this way is assumed, the new parameter satisfies to demands which are necessary to call it as additional parameter when the influence of the external actions on the material state is described thermodynamically.

The description ways of this parameters under condition of the system deviation on the equilibrium state could be various and are determined by specific physical situation.

Let analyze the multi component deformable thermodynamic system, where the mass transfer processes can proceeds. In the equilibrium state, the free energy is the function of the temperature T , strain tensor components ε_{ij} and species concentra-

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tions C_k . We will characterize the system by the additional parameter η – activation parameter (1). Then the Gibbs equation takes the form

$$du = Tds + \sigma_{ij}^e \rho^{-1} d\varepsilon_{ij} + \sum_{k=1}^n g_k dC_k - Ad\eta, \text{ J/kg} \quad (2)$$

where A is thermodynamic force which is conjugate to the additional parameter and connects to the energy need for the system activation. We have from (2)

$$T \frac{ds}{dt} = \frac{du}{dt} - \sigma_{ij}^e \rho^{-1} \frac{d\varepsilon_{ij}}{dt} - \sum_{k=1}^n g_k \frac{dC_k}{dt} + A \frac{d\eta}{dt}. \quad (3)$$

The entropy production connecting with the additional parameter evolution follows from the equality

$$\left(\frac{ds}{dt}\right)_m = \frac{A}{T} \frac{d\eta}{dt} \geq 0. \quad (4)$$

We find

$$A = T \left(\frac{\partial s}{\partial \eta}\right)_{u, \varepsilon, C_k} \quad \text{and} \quad A = - \left(\frac{\partial u}{\partial \eta}\right)_{s, \varepsilon, C_k} \quad (5)$$

from (2) and (3).

Using other forms of the Gibbs equation we can write

$$A = - \left(\frac{\partial h}{\partial \eta}\right)_{s, \sigma_{ij}^e, C_k} = - \left(\frac{\partial f}{\partial \eta}\right)_{T, \varepsilon, C_k} = - \left(\frac{\partial g}{\partial \eta}\right)_{T, \sigma_{ij}^e, C_k} \quad (6)$$

where $h = u - \sigma_{ij}^e \rho^{-1} \varepsilon_{ij}$; $f = u - Ts$; $g = u - Ts$.

Corresponding to (4), the kinetic equation describing the evolution of the additional parameter to equilibrium state can be presented in the form

$$\frac{d\eta}{dt} = L \frac{A}{T},$$

where L is the kinetic coefficient (kg·K/(J·s)). The value of the thermodynamic force A depends, naturally, on parameter η and on thermodynamic state variables, for example

$$A = A(s, \varepsilon_{ij}, C_k; \eta).$$

The constancy of those or another state parameters are determined by the specific conditions (for example, by the conditions of the external action).

In the equilibrium $A=0$, because the entropy is maximal in equilibrium conditions.

$$A_{eq} = T \left(\frac{\partial s}{\partial \eta}\right)_{eq} = 0.$$

Let expand A into the series near by the vicinity of equilibrium state with the accuracy to the items of second order of smallness in $(\eta - \eta_{eq})$. Then we shall find

$$\frac{d\eta}{dt} = \frac{L}{T} \left(\frac{\partial A}{\partial \eta}\right)_{eq} (\eta - \eta_{eq}). \quad (7)$$

Corresponding to (5), (6), we can determine different values of the derivative $(\partial A / \partial \eta)_{ed}$, relating to different the experimental conditions. For example, for (5) we have

$$\left(\frac{\partial A}{\partial \eta}\right)_{eq} = - \left(\frac{\partial^2 u}{\partial \eta^2}\right)_{s, \varepsilon_{ij}, C_k} < 0 \quad (8)$$

at the adiabatic conditions and for constant deformations and species concentrations corresponding to the equilibrium condition stability. Then from (8) we shall find

$$\eta(t) - \eta_{eq}(s, \varepsilon_{ij}, C_k) = C_1 \exp(-t/\tau_1), \quad (9)$$

where C_1 – integration constant (depending on initial deviation on the equilibrium state); τ_1 – relaxation time of parameter η to equilibrium value η_{ed} :

$$\tau_1 = \frac{T}{L} \left| \frac{1}{(\partial A / \partial \eta)_{eq}} \right| > 0. \quad (10)$$

Corresponding to (5), (6), we can determine the various relaxation time relating to the various observation conditions. One can speak, that life time of given irreversible state depends on the way which it was reached and on the following state of the system.

Note, the equation (9) can be presented in another form

$$\eta(t) - \eta_{eq} = (\eta(t) - \eta_{eq})_0 \exp[-E_a / \Pi],$$

where $E_a = m(\partial A / \partial \eta)_{ed}$ is the energy (J/mol), need for the activation of thermodynamic system to the state characterizing the current value of the additional parameter η (activation energy); $\Pi = mT/Lt$ is specific work which the system should commit to return in the equilibrium state.

Since $\eta = \eta(\sigma_{ij}^e, T, C_k)$, using the system of the thermodynamic state equations [1,7], obtaining on the base of the Gibbs equation for Gibbs, energy

$$dg_k = -\alpha_{ij}^{(k)} \rho^{-1} d\sigma_{ij}^e - s_k^{(\sigma)} dT + \sum_{j=1}^n \beta_j^{(k)} dC_j + \left(\frac{\partial g_k}{\partial \eta}\right)_{\sigma_{ab}, T, C_k} d\eta$$

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where g_k are the partial Gibbs energies of chemical potentials of components, and the differential of additional variable, which is slower or inertial than basic thermodynamic variable,

$$d\eta = \left(\frac{\partial \eta}{\partial \sigma_{ij}^e}\right) d\sigma_{ij}^e + \left(\frac{\partial \eta}{\partial T}\right) dT + \sum_{k=1}^n \left(\frac{\partial \eta}{\partial C_k}\right) dC_k,$$

we can establish, that, for the irreversible conditions, the formulae for effective properties describing by second derivatives of thermodynamic potentials, will include two items, the second of which are stipulated by the additional parameter change, that is analogous to [2].

3. The equations for mass fluxes

Omitting the intermediate computations, we write down, for example, for chemical potentials of species at the isothermal conditions

$$dg_k = - \left[\alpha_{ij}^{(k)} \rho^{-1} - \delta_k \left(\frac{\partial \eta}{\partial \sigma_{ij}^e} \right) \right] d\sigma_{ij}^e + \sum_{j=1}^n \left[\beta_j^{(k)} + \delta_k \left(\frac{\partial \eta}{\partial C_k} \right) \right] dC_k, \quad (11)$$

$$\text{where } \delta_k = \left(\frac{\partial g_k}{\partial \eta} \right) = \left(\frac{\partial^2 g}{\partial \eta \partial C_k} \right) = \left(\frac{\partial A}{\partial C_k} \right),$$

corresponding to above reasoning, is the energy need for the activation of k -species or for the evaluation of its mobility.

Taking into account the known determination of the coefficients $\beta_j^{(k)}$,

$$\beta_j^{(k)} = \frac{\partial g_k}{\partial C_j} = \frac{RT}{m_k C_k} g_{kj},$$

$$\text{where } g_{kj} = \delta_{kj} + \frac{C_k}{C_j} \frac{\partial \ln \gamma_k}{\partial \ln C_j}, \quad \text{J/kg,}$$

γ_k – are the activity coefficients for species, and Onsager's [6], we shall find at the conditions of constant stresses

$$\mathbf{J}_k = -\rho \sum_{i=1}^{n-1} D_{ki}^{(a)} \nabla C_i, \quad \text{kg/(m}^2\text{c)}, \quad (12)$$

for the mass fluxes of species, where

$$D_{ki}^{(a)} = \rho^{-1} \sum_{j=1}^n \frac{R L_{kj}}{m_j C_j} g_{ji}^{(a)},$$

$$\text{and } g_{ji}^{(a)} = g_{ji} + \delta_k \frac{m_j C_j}{RT} \left(\frac{\partial \eta}{\partial C_j} \right)$$

– partial diffusion coefficients and thermodynamic factors at the irreversible (or activated) condition; L_{kj} – phenomenological coefficients; R – universal gas constant; m_j – molar masses of species; g_{ji} – usual thermodynamic factors (the functions of species, depending on the solution or melting structure).

Taking into consideration the stresses, we shall obtain the equations for the mass fluxes

$$\mathbf{J}_k = -\rho \sum_{j=1}^{n-1} D_{kj}^{(a)} \nabla C_j + \sum_{(i,j)} B_{ij}^{(k),(a)} \nabla \sigma_{ij}^e, \quad (13)$$

where

$$B_{ij}^{(k),(a)} = \sum_{l=1}^n \alpha_{ij}^{(l),(a)} \frac{L_{kl}}{T \rho}, \quad \alpha_{ij}^{(l),(a)} = \alpha_{ij}^{(l)} - \rho \delta_l \left(\frac{\partial \eta}{\partial \sigma_{ij}^e} \right)$$

– are the transfer coefficients under stresses and the components of the tensor of concentration expansion coefficients at the irreversible condition. In the particular case of isotropic medium we have

$$\mathbf{J}_k = -\rho \sum_{j=1}^{n-1} D_{kj}^{(a)} \nabla C_j + B_k^{(a)} \nabla \sigma_{kk}^e, \quad (14)$$

instead (13), where

$$B_k^{(a)} = \sum_{l=1}^n \alpha_l^{(a)} \frac{L_{kl}}{T \rho}.$$

The equation (12–14) for the mass fluxes take a place, when the diffusion goes according to interstitial mechanism. It is not difficult to write down the analogous equation for the diffusion by vacancy mechanism.

4. Ideal and non-ideal solutions

The correlation between the diagonal Onsager coefficients L_{kk} and self-diffusion coefficients D_k^*

$$L_{kk} = (\rho D_k^* C_k m_k) / R, \quad (15)$$

is established in the diffusion theory. That allows, using the simplest approximations of ideal and non-ideal solutions, to determine the formulae for the partial diffusion coefficients.

So, for binary system (for the system consisting of two different species), we can write

$$\mathbf{J}_k = -\rho D_k^{(a)} \nabla C_k, \quad k=1,2, \quad (16)$$

where

$$D_k^{(a)} = D_k^* g_{kk}^{(a)}, \quad g_{kk}^{(a)} = 1 + \frac{\partial \ln \gamma_k}{\partial \ln C_k} + \delta_k \frac{m_k C_k}{RT} \frac{\partial \eta}{\partial C_k}. \quad (17)$$

In the case of triply system with the concentrations C_1, C_2, C_3 two equations for the mass fluxes

$$\mathbf{J}_1 = -\rho (D_{11}^{(a)} \nabla C_1 + D_{12}^{(a)} \nabla C_2),$$

$$\mathbf{J}_2 = -\rho (D_{21}^{(a)} \nabla C_1 + D_{22}^{(a)} \nabla C_2),$$

where

$$D_{ij}^{(a)} = \frac{R}{\rho} \sum_{k=1}^3 L_{ik} \frac{g_{kj}^{(a)}}{m_k C_k}, \quad i, j=1,2 \quad (18)$$

are enough to describe in the diffusion.

Two types of the approximation are applied in the diffusion theory by interstitial mechanism. In the first case, ones assume that the solution is ideal. That corresponds to small concentrations of solved species in the dissolvent, so the interrelation between solved substances is negligible small. Than $(\partial \ln \gamma_j / \partial \ln C_j) = 0$. By analogy, assuming, that $(\partial \eta / \partial C_j) = 0, j \neq i$ in (17), we shall find

$$D_{11} = D_1^* g_{11}^{(a)}, \quad D_{12} = \frac{R}{\rho} \frac{L_{12}}{m_2 C_2} g_{11}^{(a)},$$

$$D_{21} = \frac{R}{\rho} \frac{L_{21}}{m_1 C_1} g_{22}^{(a)} \neq D_{12}, \quad D_{22} = D_2^* g_{22}^{(a)}$$

instead the coefficient system (18).

Non-ideal solutions are examined in another approximation: ones assume that it is permissible to neglect the cross coefficients $L_{ij}, i \neq j$ in comparison with diagonal coefficients L_{ii} , if the diffusion goes by interstitial mechanism, that has been grounded in the statistic physics. In this case, the diffusion coefficient system is simplified also, but differs from previous one

$$D_{11} = D_1^* g_{11}^{(a)}, \quad D_{12} = D_1^* g_{12}^{(a)},$$

$$D_{21} = D_2^* g_{21}^{(a)}, \quad D_{22} = D_2^* g_{22}^{(a)}.$$

It is not difficult to show that these two approximations give for multi component system the equations for fluxes (12) with the coefficients

$$D_{kk} = D_k^{(a)} = D_k^* g_{kk}^{(a)} \quad \text{and} \quad D_{kj}^{(a)} = D_{kj}^0 g_{kk}^{(a)} \quad (k \neq j),$$

where D_{kj}^0 are the partial diffusion coefficients for no activated state, for ideal solution, and

$$D_{kj}^{(a)} = D_k^* g_{kj}^a$$

– for non-ideal solution.

5. Tensor concentrations

The expansion of the approach for the description of the irreversible diffusion in chemical compounds it is possible using the conceptions of tensor concentrations $C_{ij}^{(k)}$ [7]. In this case, the chemical potentials of species $k_j^{(k)}$ are tensors of second rank and the third item of the equation (2) takes the form

$$\sum_{k=1}^n \sum_{(i,j)} g_{ij}^{(k)} dC_{ij}^{(k)}.$$

The structure of these tensors and the number of their independent components are determined by the symmetry type of the crystal lattice of real substances. The simple generalization of the chemical potential determination gives for the corresponding tensor components the formula

$$(dg_{ij}^{(k)})_{T,\sigma} = \frac{RT}{m_k} d \ln [C_{ij}^{(k)} \gamma_{ij}^{(k)}]$$

and leads to tensors of concentration expansion coefficients of the fourth rank; tensor partial entropies and energies need for the activation. Obviously, these energetic parameters should be connected with the chemical bonds energies in the crystal sublattices forming by the atoms of each kind. The computations becomes more cumbersome.

6. Conclusion

So, it is possible to describe the mass transfer coefficients and mechanism change at the irreversible conditions in term of irreversible continual thermodynamics.

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