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JOINT DIFFUSION IN INTERSTITIAL SOLUTIONS

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Within the framework of the simplest model of a two-component solid solution the article examines the dependence of the diffusion fluxes of implanted substances on their concentration and on the inhomogeneity of the lattice composition. It is shown that cross effects lead to contributions that are comparable in magnitude to the principal fluxes.

In the practice of thermochemical treatment of metals and alloys, and in particular in processes of case-hardening and nitriding, situations are ordinarily encountered where the introduction of an additional admixture to a system substantially changes the rate of mass transfer and the kinetics of saturation of the material with the principal diffusing substance. For instance, the addition of nitrogen is able to accelerate the transfer of carbon to more than twice the original rate, the same effect is found when a phase contains ammonia, methane, or some other gases (see, e.g., [1, 2]). Under certain conditions mass transfer is even possible in the direction of the gradient of concentration of the substance. Although the fundamental cause of such "ascending" or "negative" diffusion is not difficult to understand, e.g., on the basis of Darken's phenomenological theory [3, 4], such a strong effect of implanted admixtures on the diffusion of any of them still lacks of a physical explanation on the example of the simplest possible model. A physical analysis of this kind is carried out below for a two-component interstitial solid solution within the framework of an atomic model in which we neglect the existence of an electron subsystem and the deformations of the crystal lattice of a metal or an interstitial alloy; only the statistical configurational properties of the system and the interaction energy of pairs of atoms in the nodes and internodes of the lattice were taken into account.

We will assume that both kinds of interstitial atoms fill the same type of internodes forming a regular lattice with the coordination number γ, and that each internode borders on z nodes of the basic crystal lattice which may be free (with a probability $m_v = M_v/M$) or filled with J various types of atoms (with the probability $m_j = M_j/M$, $j = 1, \ldots, J$). We assume that the composition of the alloy, i.e., the numbers M_j and M_v, are known and that they do not change during the process of diffusion. This last corresponds to the assumption that the diffusion coefficients of interstitial atoms are much larger than these coefficients for vacancies and atoms in the nodes of the basic lattice.

We represent the interaction energy of the interstitial atoms between each other and with the atoms in the nodes per unit volume in the form

$$E = \sum_{j=1}^{J} (\varepsilon_1^j M_{1j} + \varepsilon_2^j M_{2j}) + \varepsilon_{11} N_{11} + \varepsilon_{12} N_{12} + \varepsilon_{22} N_{22}, \tag{1}$$

where M_{ij} is the concentration of bonds of interstitial atoms of i-th type with atoms of j-th type in the nearest nodes; N_{ik} is the concentration of bonds of interstitial atoms of the i-th and k-th types in the neighboring internodes. Formula (1) corresponds to the approximation of the nearest neighbors.

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At present we will not carry out a rigorous calculation of the numbers M_{ij} and N_{ik}, they can be estimated on the basis of approximate models. To obtain conclusions of a fundamental nature, we use here the simplest model in which any ordering, both in the alloy and in the solution, is completely neglected; this corresponds to the known Bragg–Williams approximation. Then

$$M_{ij} = zN_i\frac{M_j}{M},\quad N_{ii} = \frac{\gamma}{2}\frac{N_i^2}{N},\quad N_{ik} = \gamma\frac{N_iN_k}{N}\quad (i \neq k),$$

i.e., it follows from (1) that

$$E = \frac{z}{M}\sum_{j=1}^{J}(\varepsilon_1^j N_1 + \varepsilon_2^j N_2)M_j + \frac{\gamma}{N}\left(\varepsilon_{11}\frac{N_1^2}{2} + \varepsilon_{12}N_1N_2 + \varepsilon_{22}\frac{N_2^2}{2}\right). \tag{2}$$

The number of physically different configurations of the system of two types of interstitial atoms in the lattice of internodes for $N_i \gg 1$ is equal to

$$W = \frac{N!}{N_1!N_2!(N - N_1 - N_2)!} \approx \left(\frac{N_1}{N}\right)^{-N_1}\left(\frac{N_2}{N}\right)^{-N_2}\left(1 - \frac{N_1 + N_2}{N}\right)^{-N+N_1+N_2}. \tag{3}$$

The free Helmholtz energy of this system can be represented in the form

$$\begin{aligned} F = F^\circ - kT\ln[W\exp(-E/kT)] = z\sum_{j=1}^{J}(\varepsilon_1^j N_1 + \varepsilon_2^j N_2)\frac{M_j}{M} + \\ + \gamma\left(\varepsilon_{11}\frac{N_1^2}{2} + \varepsilon_{12}N_1N_2 + \varepsilon_{22}\frac{N_2^2}{2}\right)\frac{1}{N} + \\ + \left[(N - N_1 - N_2)\ln\frac{N - N_1 - N_2}{N} + N_1\ln\frac{N_1}{N} + N_2\ln\frac{N_2}{N}\right] \end{aligned} \tag{4}$$

(relations (2) and (3) were used). Since the change of volume of the crystal lattice upon the implanting of dissolved atoms was neglected, the free energy (4) coincides with the thermodynamic Gibbs potential; from (4) therefore follow expressions for the chemical potentials of both types of interstitial atoms:

$$\begin{aligned} \mu_1 &= \mu_1^\circ + z\sum_{j=1}^{J}\varepsilon_1^j m_j + \gamma(\varepsilon_{11}n_1 + \varepsilon_{12}n_2) + kT\ln\frac{n_1}{1 - n_1 - n_2}, \\ \mu_2 &= \mu_2^\circ + z\sum_{j=1}^{J}\varepsilon_2^j m_j + \gamma(\varepsilon_{22}n_2 + \varepsilon_{12}n_1) + kT\ln\frac{n_2}{1 - n_1 - n_2}, \\ & m_j = M_j/M,\quad n_i = N_i/N. \end{aligned} \tag{5}$$

In (4) and (5) a degree sign as superscript denotes the components not connected with the distribution of atoms in internodes and with interatomic interaction; these components do not depend on n_i, m_j.

In accordance with the linear thermodynamics of irreversible processes, the diffusion fluxes can be represented as follows:

$$\mathbf{Q}_i = -T\sum_k L_{ik}\nabla\left(\frac{\mu_k}{T}\right).$$

It follows from the requirements of increasing entropy in an irreversible process and the microscopic reversibility of elementary displacements that in the absence of rotation and of an external magnetic field, the Onsager coefficients L_{ik} form a positively determined quadratic shape and are symmetrical; otherwise the values of L_{ik} not depending on thermodynamic forces are arbitrary. In the presented case it appears that the matrix of these coefficients also has to be diagonal. In fact, if under isothermal conditions thermodynamic equilibrium is attained for the i-th component (T = const, μ_i = const), then the flux Q_i, which is due to the imbalance of the distribution of the other components of the solution, is bound to be of the order of an infinitesimal in regard to thermodynamic forces higher than first order. It is clear that taking such a flux into account within the framework of a linear theory, which Onsager's theory is, would exceed the accuracy of the latter. The cross coefficients L_{ik} therefore have to be adopted equal to zero. We want to point out that this simple consideration in no way contradicts the existence of other cross effects. For instance, the appearance of thermodiffusion with n_i = const is due to the absence of equilibrium in regard to this same i-th component ($\mu_i/T \neq$ const).

When diffusion in solids is investigated, in most cases the cross effects are neglected, and it is usual to put $L_{ik} = 0$, $i \neq k$; the correctness of such a simplication is indirectly confirmed by the adequacy of Darken's theory, the insignificance of the Manning effect, and a number of other known facts [3, 4]. We therefore adopt below for isothermal conditions:

$$\mathbf{Q}_i = -L_i \nabla \mu_i, \quad i = 1,\ 2. \tag{6}$$

Using in (6) the expressions for the chemical potentials from (5), we obtain the relations

$$\mathbf{Q}_i = -\sum_{k=1}^{2} D_{ik} \nabla n_k + \mathbf{Q}_i^*, \tag{7}$$

where we introduce the diffusion coefficients

$$\begin{gathered} D_{ii} = L_i\left[\gamma\varepsilon_{ii} + kT\left(\frac{1}{n_i} + \frac{1}{1 - n_1 - n_2}\right)\right], \quad i = 1,\ 2, \\ D_{12} = L_1\left(\gamma\varepsilon_{12} + \frac{kT}{1 - n_1 - n_2}\right), \quad D_{21} = L_2\left(\gamma\varepsilon_{12} + \frac{kT}{1 - n_1 - n_2}\right) \end{gathered} \tag{8}$$

and the additional fluxes due to the inhomogeneity of the alloy

$$\mathbf{Q}_i^* = -zL_i \sum_{j=1}^{J} \varepsilon_i^j \nabla m_j, \quad i = 1,\ 2. \tag{9}$$

Thus the matrix of the diffusion coefficients is optionally symmetrical. Expressions (7) and (8) differ substantially from the expressions following from (6) when for the chemical potentials of the dissolved substances in a nonideal solution not (5) is used but the standard representations in the form

$$\mu_i = \mu_i^\circ + kT \ln(\gamma_i n_i),$$

where γ_i are the coefficients of activity. We therefore point out that such notions seem natural only when the deviations of the solution from the ideal state are small, i.e., $n_i \ll 1$, $|\varepsilon_{ik}|/kT \ll 1$ and $|\varepsilon_i^j|/kT \ll 1$. To require that the last two inequalities be fulfilled is inexpedient even in the case of dilute solid solutions because the determination of the solid state of aggregation itself reduces in effect to the condition that kT be small in comparison with the characteristic interaction energy, i.e., in reality the inverse strong inequalities $|\varepsilon_{ik}|kT \gg 1$ and $|\varepsilon_i^j|/kT \gg 1$ are probable.

For the diffusion coefficients expressions (8) imply that the diffusion of interstitial atoms is stimulated by two physical factors of different nature. The appearance of terms with kT corresponds to the natural tendency of the system of interstitial atoms toward a chaotic state corresponding to the maximal configurational entropy, the appearance of terms with ε_{ik} (like the origin of additional fluxes Q_i^*) expresses the endeavor of the system to assume a state with minimal interaction energy.

To evaluate the order of the cross diffusion coefficients, it is expedient to eliminate the coefficients L_i from (8). Then we obtain

$$D_{12} = D_{11}\,\frac{\gamma\varepsilon_{12} + kT(1 - n_1 - n_2)^{-1}}{\gamma\varepsilon_{11} + kT[n_1^{-1} + (1 - n_1 - n_2)^{-1}]},$$
$$D_{21} = D_{22}\,\frac{\gamma\varepsilon_{12} + kT(1 - n_1 - n_2)^{-1}}{\gamma\varepsilon_{22} + kT[n_2^{-1} + (1 - n_1 - n_2)^{-1}]}. \tag{10}$$

The limit relations for ideal solutions with small concentration ($n_i \ll 1$, $\varepsilon_{ik} = 0$) have the form

$$D_{12} \approx n_1 D_{11},\quad D_{21} \approx n_2 D_{22}, \tag{11}$$

i.e., the cross effects in this case are in fact weak. In the opposite case, when $\gamma|\varepsilon_{ik}| \gg n_i kT$, we have

$$D_{12} \approx (\varepsilon_{12}/\varepsilon_{11})\,D_{11},\quad D_{21} \approx (\varepsilon_{12}/\varepsilon_{22})\,D_{22}, \tag{12}$$

and this case is probable even with small n_i, i.e., for dilute interstitial solid solutions.

Thus it can be seen from (10) and (12) that the cross fluxes $-D_{12}\nabla n_2$ and $-D_{21}\nabla n_1$ in a two-component interstitial solution have, generally speaking, the same order of magnitude as the principal fluxes $-D_{11}\nabla n_1$ and $-D_{22}\nabla n_2$. Here the coefficients D_{12} and D_{11} or D_{21} and D_{22} may have the same sign or different signs in dependence on the signs of the energies ε_{12}, ε_{11}, and ε_{22}. This last is particularly important in the analysis of systems with Coulomb interaction, i.e., in the diffusion, not of electrically neutral interstitial atoms, but of ions; this is important for mass exchange processes, not only in metals or alloys, but also in other crystalline systems, in molten ionic salts, etc.

Expressing L_i through D_{ii} in accordance with (8) and using the results in (9), we can obtain relations for additional fluxes due to the inhomogeneity of the prinicpal crystal lattice. We have

$$\mathbf{Q}_i^* = -\sum_{j=1}^{J} D_{ij}^*\nabla m_j, \tag{13}$$

where for D_{ij}^* relations analogous to (10) are correct:

$$D_{ij}^* = D_{ii}\,\frac{z\varepsilon_i^j}{\gamma\varepsilon_{ii} + kT[n_i^{-1} + (1 - n_1 - n_2)^{-1}]}. \tag{14}$$

Hence, in analogy to the preceding, the general conclusion follows that the order of magnitude of the coefficients D_{ij}^* is, generally speaking, the same as the order of the principal diffusion coefficients D_{ii}.

In diffusion in pure metal (J = 1) we have $\nabla m_1 = -\nabla m_v$, i.e., instead of (13) and (14) we obtain

$$\mathbf{Q}_i^* = -D_i^*\nabla m_v,\quad D_i^* = -D_{ii}\,\frac{z\varepsilon_i^1}{\gamma\varepsilon_{ii} + kT[n_i^{-1} + (1 - n_1 - n_2)^{-1}]}. \tag{15}$$

Thus there appears a flux of interstitial atoms directly correlated with the gradient of vacancy concentration. Depending on the signs of the interaction energy, the flux may either cause or inhibit the shifting of atoms through regions in which this concentration is very nonuniform. This last has a direct bearing, e.g., on processes of the penetration of insterstitial atoms from intergranular interlayers into the grains of polycrystalline metals; under certain conditions the flux may be completely stopped in spite of a concentration gradient of the diffusing substance.

The obtained conclusions do not change fundamentally when the theory is refined by using Kirkwood's approximation, the quasichemical (Bete—Peierls) approximation, etc. Their detailed comparison with accumulated experimental data will be discussed later. Here we note solely that these conclusions correspond qualitatively quite well to many observed facts and permit the assumption of a natural interpretation of a number of phenomena that had hitherto not been explained.

In conclusion, we emphasize that the existence of the examined cross effects must be taken into account in the processing of experiments involving diffusion; this has usually not been done so far. It will then be possible to avoid the introduction of unrealistically high coefficients of activity of diffusing substances, the known indeterminacies in determining the diffusion coefficients in multicomponent systems, etc.

NOTATION

D_{ik}, D^*_{ij}, diffusion coefficients; E, interaction energy of interstitial atoms; F, free energy; k, Boltzmann constant; L_{ik}, Onsager coefficients; M, M_v, M_j, concentrations of nodes of the crystal lattice, of vacancies, and of the j-th type of atoms in the lattice; M_{ij}, volumetric concentration of bonds of the i-th interstitial atoms with the j-th atoms in the lattice; m_v, m_j, proportions of nodes occupied by vacancies and the j-th type of atoms, respectively; N, N_i, concentrations of internodes and interstitial atoms of the i-th type, respectively; n_i, proportion of internodes occupied by i-th type of atoms; Q_i, diffusion flux of the i-th interstitial atoms; Q^*_i, part of Q_i due to the nonuniformity of the lattice; T, absolute temperature; z, number of neighboring nodes at an internode; γ, coordination number of the internodes; ε_{ik}, interaction energy of i-th and k-th types of interstitial atoms in neighboring internodes; ε^j_i, interaction energy of an i-th type interstitial atom with a j-th type atom in a neighboring node; μ_i, chemical potential of an i-th type atom.

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