Modeling of Intergrain Diffusion in Solids with Account for Grain Surface Morphology

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Abstract–An equation for intergrain diffusion accounting for grain surface topology has been derived. The diffusion tensor is proportional to the topological tensor. The extreme properties of the generalized diffusion coefficient in a one-dimensional equation have been studied by means of an approximation of grain surfaces.

Some properties of protective coatings on substrates are controlled by the diffusion rate of an impurity in the coating. For example, the bioinertness of coatings on implants depends on the diffusion rate of the implant material through the protective layer to living tissues. The aforementioned diffusion is frequently controlled by grain-boundary diffusion. Therefore, it is important to recognize the parameters that affect intergrain diffusion. For example, presumably, the grain size of the layer material affects intergrain diffusion. We will show that, when intergrain distances are far smaller than grain sizes, diffusion depends on the specific grain surface gradient and the generalized diffusion tensor is proportional to the topological tensor.

DERIVATION OF AN EQUATION FOR INTERGRAIN DIFFUSION WITH ACCOUNT FOR GRAIN TOPOLOGY

In deriving the diffusion equation, we will use notations employed in the derivation of averaged equations of heterogeneous mechanics [1]. Let dV be a representative volume of the medium (Fig. 1) containing many grains (a representative number of grains), dS be the surface bounding volume dV, $\vec{N}$ the unit normal to surface dS, dS_{12} the grain surface area in representative volume dV, and s_{12} the specific grain surface:

$$s_{12} = \frac{dS_{12}}{dV}. \qquad (1)$$

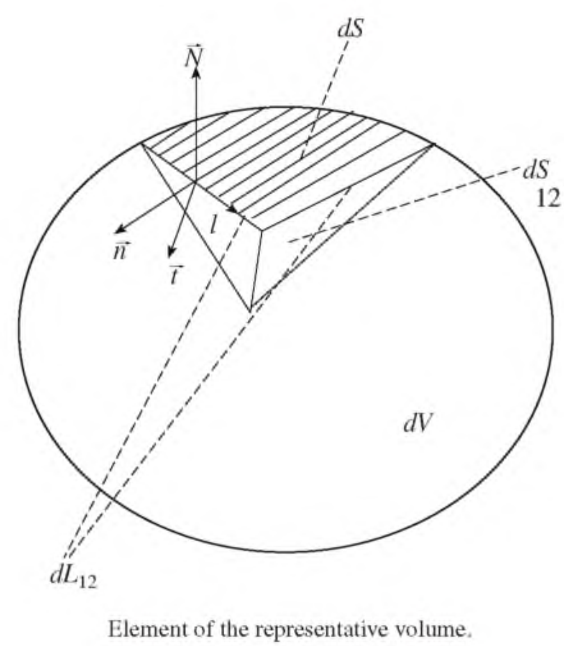
Indexes 1 and 2 refer to grain and intergrain phases, respectively.

Let us write the mass conservation law for an impurity diffusing through the intergrain space. Let diffusion occur along grain surfaces in the near-surface layer with the thickness $\Delta \ll L$, where L is the characteristic grain size, and let the impurity concentration gradient in the direction normal to grain surfaces be ignorable compared to the gradient in the direction tangential to grain surfaces. A change in the impurity weight in volume dV is due to the diffusion flow of the impurity through surface $dS_2 \subset dS$, where dS_2 is the intersection of surface dS with the intergrain region of volume dV. For simplicity, we ignore the change in the impurity weight due to convection through surface dS_2. The aforementioned mass conservation law reads

$$\frac{\partial}{\partial t}(s_{12}\rho_S dV\Delta) = \int\limits_{dS_2} D(\vec{N}\vec{\nabla}'\rho')d'S, \qquad (2)$$

where the average impurity density in the intergrain phase is denoted as

$$\rho_S = \langle\rho'\rangle_{12} = \frac{1}{dS_{12}}\int\limits_{dS_{12}} \rho'\Delta d'S. \qquad (3)$$



Element of the representative volume.

Primes in Eqs. (2) and (3) and hereafter denote local values [1] as distinct from average parameters, which depend on the coordinates of the representative volume. Surface dS_2 is a narrow strip on surface dS lying along line dL_{12}, which is the intersection of surface dS with grain-boundary surfaces. The width of the δ projection Δ on surface dS is far smaller than the characteristic grain size L. In view of the narrowness of surface dS_2, we replace integration over surface dS_2 in the right-hand side of Eq. (2) by integration along lines dL_{12}. Evidently, with account for $(\vec{N}\vec{l}') = 0$ (where $\vec{l}'$ is the unit tangential vector to dL_{12}), normal $\vec{N}$ can be represented as

$$\vec{N} = (\vec{N}\vec{\tau}')\vec{\tau}' + (\vec{N}\vec{n}')\vec{n}'.$$

Here, $\vec{n}'$ is the unit normal to the grain surface and $\vec{\tau}' = \vec{l}' \times \vec{n}'$. Therefore, $(\vec{N}\vec{\nabla}'\rho') = (\vec{N}\vec{\tau}')(\vec{\tau}'\vec{\nabla}'\rho') + (\vec{N}\vec{n}')(\vec{n}'\vec{\nabla}'\rho')$. Ignoring the impurity density gradient in the direction normal to the grain surface compared to the tangential gradient from the last equality, we obtain

$$(\vec{N}\vec{\nabla}'\rho') = (\vec{N}\vec{\tau}')(\vec{\tau}'\vec{\nabla}'\rho'). \tag{4}$$

Taking into account Eq. (4) and that $d'S = \delta d'l = \Delta d'l/(\vec{N}\vec{\tau}')$, we write the right-hand side of Eq. (2) as follows:

$$\int\limits_{dS_2} D(\vec{N}\vec{\nabla}'\rho')d'S = \int\limits_{dL_{12}} D\Delta(\vec{\tau}'\vec{\nabla}'\rho')d'l. \tag{5}$$

We calculate integral (5) using additional spatial averaging [2], i.e., by averaging the integral in the direction of normal $\vec{N}$ to the surface dS of representative volume dV. The additional averaging of integral (5) is carried out over distance ΔN, which has the same order of magnitude of the grain size, as follows:

$$\begin{aligned} &\frac{1}{M}\sum_{i=1}^{M}\int\limits_{dL_{12i}} D\Delta(\vec{\tau}'\vec{\nabla}'\rho')d'l \\ &= \frac{1}{M\delta N}\sum_{i=1}^{M}\delta N\int\limits_{dL_{12i}} D\Delta(\vec{\tau}'\vec{\nabla}'\rho')d'l \\ &= \frac{1}{\Delta N}\sum_{i=1}^{M}\int\limits_{dL_{12i}} D\Delta(\vec{\tau}'\vec{\nabla}'\rho')(\vec{\tau}'\vec{N})\,d'\tau d'l \\ &= \frac{1}{\Delta N}\int\limits_{dS_{12N}} D\Delta(\vec{\tau}'\vec{\nabla}'\rho')(\vec{\tau}'\vec{N})d'S. \end{aligned} \tag{6}$$

Here, we account for the fact that $d'S = d'\tau d'l$ and integration takes place over grain surface dS_{12N} contained in the layer with thickness ΔN near surface dS, which bounds representative volume dV. In further calculations, we will set that the diffusion coefficient D and the thickness of the near-surface layer Δ to be constant. We use standard notations for integrals over the interface from [1]:

$$s_{12}\langle(\vec{\tau}'\vec{\nabla}'\rho')(\vec{\tau}'\vec{N})\rangle_{12} = \frac{1}{dS_{12}}\int\limits_{dS_{12}}(\vec{\tau}'\vec{\nabla}'\rho')(\vec{\tau}'\vec{N})d'S. \tag{7}$$

Substituting the right-hand side in the form of Eq. (6) into Eq. (2) and using notation (7), we obtain the mass conservation equation for the impurity in the form

$$\frac{\partial}{\partial t}(s_{12}\langle\rho'\rangle_{12}dV\Delta) = D\int\limits_{dS}\Delta\vec{N}s_{12}\langle(\vec{\tau}'\vec{\nabla}'\rho')\vec{\tau}'\rangle_{12}d'S. \tag{8}$$

Integrating the right-hand side of Eq. (8) over volume dV and setting Δ constant, we obtain the mass conservation equation for an impurity in the form

$$\frac{\partial}{\partial t}(s_{12}\langle\rho'\rangle_{12}) = D\mathrm{div}(s_{12}\langle(\vec{\tau}'\vec{\nabla}'\rho')\vec{\tau}'\rangle_{12}). \tag{9}$$

Next, we transform the right-hand side of Eq. (9). From evident geometric considerations (Fig. 1),

$$\tau'^p\tau'^q = \delta^{pq} - n'^p n'^q. \tag{10}$$

We write Eq. (9) using equality (10) as

$$\frac{\partial}{\partial t}(s_{12}\langle\rho'\rangle_{12}) = D\nabla^p(s_{12}\langle(\delta^{pq} - n'^p n'^q)\nabla'^q\rho'\rangle_{12}), \tag{11}$$

introducing a notation for the partial derivative operator: $\nabla^p = \dfrac{\partial}{\partial x^p}$. For further purposes, we transform the right-hand side of Eq. (11). We take into account that the magnitude of the unit normal is unity; the mean curvature of the planar intergrain surface is nullified:

$$\frac{1}{R_1'} + \frac{1}{R_2'} = \mathrm{div}'\vec{n}' = \nabla'^q n'^q = 0.$$

Here, R_1' and R_1' are the local principal radii of curvature of the surface; the normal impurity concentration gradient is ignorable compared to the tangential gradient. Then,

$$\begin{aligned} (\delta^{pq} - n'^p n'^q)\nabla'^p\rho' &= n'^q n'^q\nabla'^p\rho' - n'^q n'^p\nabla'^q\rho' \\ &= [n'^q\nabla'^p(n'^q\rho') - n'^p\nabla'^q(n'^q\rho')] \\ &+ n'^p\nabla'^q(n'^q\rho') - \rho' n'^q\nabla'^p(n'^q) - n'^p n'^q\nabla'^q\rho' \\ &= (n'^q\nabla'^p - n'^p\nabla'^q)(n'^q\rho') = ((\vec{n}'\times\vec{\nabla}')\times(\vec{n}'\rho'))^p. \end{aligned} \tag{12}$$

We use an analogue of the Stokes relationship for heterogeneous media [3] (here, as in [3], integrals over the lines bounding crystallite facets inside volume dV are cancelled out, because they are passed in opposite directions during integration):

$$s_{12}\langle(\vec{n}'\times\vec{\nabla}')\times(\vec{n}'\rho')\rangle_{12} = \nabla^q(s_{12}\langle(\vec{n}'\rho')\times(\vec{e}^q\times\vec{n}')\rangle_{12}). \quad (13)$$

Substituting Eq. (12) into the right-hand side of Eq. (11), using Eq. (13), and carrying out obvious transformations, we obtain the following mass conservation equation for the impurity:

$$\frac{\partial}{\partial t}(s_{12}\langle\rho'\rangle_{12}) = D[\mathrm{div}\vec{\nabla}(s_{12}\langle\rho'\rangle_{12}) - \mathrm{div}\nabla^q(s_{12}\langle\rho' n'^q\vec{n}'\rangle_{12})]. \quad (14)$$

For further calculations, we use the topological hypothesis, whose essence is described in detail in [3]; this hypothesis holds if there exists a distribution function of the specific interface area versus the tilting angles of its normal. In the case at hand, the topological hypothesis leads to the equality

$$s_{12}\langle\rho' n'^q\vec{n}'\rangle_{12} = s_{12}\langle\rho'\rangle_{12}\langle n'^q\vec{n}'\rangle_{12}. \quad (15)$$

Substituting equality (15) into Eq. (14) and carrying out simple transformations, we obtain the mass conservation equation for the impurity in the form of the diffusion equation as follows:

$$\frac{\partial}{\partial t}(s_{12}\rho_S) = \nabla^p\nabla^q(D^{pq}s_{12}\rho_S), \quad D^{pq} = D(\delta^{pq} - \nu^{pq}). \quad (16)$$

Here,

$$\nu^{pq} = \langle n'^p n'^q\rangle_{12}, \quad (17)$$

where $\frac{1}{2}(\delta^{pq} - \nu^{pq})$ is the topological tensor (evidently, its trace is unity) and D^{pq} will be called the generalized diffusion tensor, which accounts for the grain surface topology. Tensor $s^{pq} = \frac{1}{2}s_{12}(\delta^{pq} - \nu^{pq})$ is the specific area tensor [2]; its trace is s_{12}, the specific grain surface area. Evidently, $s_{12}\rho_S = \rho_V$ is the impurity density in volume dV.

DIFFUSION EQUATION FOR THE CASE OF CONSTANT SPECIFIC SURFACE AREAS AND CONSTANT TOPOLOGICAL TENSOR TERMS

We write Eq. (16) for the case where the terms of the topological tensor are constant. Then, Eq. (16) is simplified and acquires the form

$$\frac{\partial\rho_V}{\partial t} = D^{pq}\Sigma\nabla^p\nabla^q\rho_V. \quad (18)$$

Note. From the form of Eq. (18) and the constancy of the topological tensor, it follows that, in the coordinate system in which the topological tensor has a diagonal form, Eq. (18) acquires the canonical form

$$\frac{\partial\rho_V}{\partial t} = D((1-\nu^{11})\nabla^1\nabla^1\rho_V + (1-\nu^{22})\nabla^2\nabla^2\rho_V + (\nu^{11}+\nu^{22})\nabla^3\nabla^3\rho_V), \quad (19)$$

which accounts for the fact that $1 - \nu^{33} = \nu^{11} + \nu^{22}$. All factors at the spatial derivatives in Eq. (19) are positive, as follows from the definition of topological tensor terms (17). Therefore, the differential operator in the right-hand side is elliptical. Equation (19) can be further simplified using new spatial variables, namely,

$$\tilde{x}^1 = x^1/\sqrt{1-\nu^{11}}; \quad \tilde{x}^2 = x^2/\sqrt{1-\nu^{22}}; \quad \tilde{x}^3 = x^3/\sqrt{\nu^{11}+\nu^{22}}. \quad (20)$$

Then, Eq. (19) in the new coordinates (marked with a tilde) acquires the standard form of the diffusion equation:

$$\frac{\partial\rho_V}{\partial t} = D\Delta\rho_V. \quad (21)$$

As an example, let us derive Eq. (19) for a model case, setting the approximation of grain surfaces. We can propose a method for approximate calculations of topological tensor terms. This method consists of the following: the real grain surface is fitted by a simpler one for which topological tensor terms can be calculated. For example, the grain surface is fitted by identical parallelotopes. Let parallelotopes have lengths, widths, and heights of $a \geq b \geq c$, respectively. The normal to the surface (a, b) of the parallelotope is denoted as $\vec{n} = \{\sin\theta\cos\phi, \sin\theta\cos\phi, \cos\theta\}$. Here, θ is the angle formed by the normal and axis 3 in the Cartesian coordinates. Angle ϕ in the plane normal to axis 3 in the Cartesian coordinates is counted from direction 1 to the projection of the long side a of a parallelotope on plane (1, 2) in the Cartesian coordinates. Let θ = const and ϕ = const for all parallelotopes (they are packed identically); then, the terms of the topological tensor are constant. Let us consider a one-dimensional problem where only the derivatives in direction 3 in the diffusion equation are not null and the derivatives with respect to coordinates x^1 and x^2 are null. Diffusion equation (19) acquires the form

$$\frac{\partial\rho_V}{\partial t} = D(1-\nu^{33})\nabla^3\nabla^3\rho_V. \quad (22)$$

We determine the topological tensor term $\frac{1}{2}(1-\nu^{33})$ in the case at hand where grain surfaces are fitted by parallelotope surfaces. For this purpose, we determine, on axis 3, the terms of the normals to parallelotope planes (a, c) and (b, c). For the directrices of the sides of the parallelotope, we have the following evident equalities:

$$\begin{aligned} \vec{c} &= c\vec{n} = c\{\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta\}, \\ \vec{a} &= a\{\sin\gamma\cos\psi, \sin\gamma\sin\psi, \cos\gamma\}, \\ \vec{b} &= b\frac{\vec{c}\times\vec{a}}{|\vec{c}\times\vec{a}|}. \end{aligned} \tag{23}$$

Here, γ is the angle formed by edge a and axis 3, ψ is the angle formed by the projection of edge a on plane (1, 2) and axis 1. Because the scalar product of the orthogonal vectors $\vec{a}\vec{c} = 0$, from this and from (23),

$$\begin{aligned} \cos(\phi-\psi) &= -\cot\theta\cot\gamma; \\ b^3 &= b\sin\theta\sin\gamma\sin(\phi-\psi). \end{aligned} \tag{24}$$

Then, for a term of the topological tensor, we obtain the equality

$$\begin{aligned} \frac{1}{2}(1-\nu^{33}) &= \frac{1}{2}\left(1-\frac{2\cos^2\theta S_{ab}+2\sin^2\theta\sin^2\gamma\sin^2(\phi-\psi)S_{ac}+2\cos^2\gamma s_{bc}}{2(S_{ab}+S_{ac}+S_{bc})}\right) \\ &= \frac{1}{2}\left(1-\frac{\frac{1}{\tilde{c}}\cos^2\theta+\frac{1}{\tilde{b}}\cos(\gamma-\theta)\cos(\gamma+\theta)+\cos^2\gamma}{1+\frac{1}{\tilde{b}}+\frac{1}{\tilde{c}}}\right). \end{aligned} \tag{25}$$

Here, the surface areas of parallelotope faces are $S_{ab} = ab$, $S_{bc} = bc$, and $S_{ac} = ac$ and the dimensionless width and height are $\tilde{b} = b/a$ and $\tilde{c} = c/a$, respectively. We denote

$$\begin{aligned} D_\Sigma &= D(1-\nu^{33}) \\ &= D\left(1-\frac{\frac{1}{\tilde{c}}\cos^2\theta+\frac{1}{\tilde{b}}\cos(\gamma-\theta)\cos(\gamma+\theta)+\cos^2\gamma}{1+\frac{1}{\tilde{b}}+\frac{1}{\tilde{c}}}\right). \end{aligned} \tag{26}$$

Let D_Σ be the generalized diffusion coefficient that accounts for the grain surface topology. From Eq. (26) for the generalized diffusion coefficient, we can see that it depends on the orientation of parallelotopes (which is determined by two angles θ and γ) and two dimensionless parameters (parallelotope width and height $\tilde{b}$ and $\tilde{c}$, respectively). These four parameters (θ, γ, $\tilde{b}$, and $\tilde{c}$) in the model that approximates grain surfaces by parallelotopes can be parameters of the diffusion-controlling process. We can increase or decrease diffusion by changing θ, γ, $\tilde{b}$, and $\tilde{c}$. From the parameters of this model, $1 \ge \tilde{b} \ge \tilde{c}$, $0 \le \theta \le \pi/2$, and $\pi/2 - \theta \le \gamma \le \pi/2$. Let us examine D_Σ for extremes as a function of θ and γ, with the dimensionless parallelotope width $\tilde{b}$ and parallelotope height $\tilde{c}$ set to be constant. Differentiating Eq. (26), we obtain

$$\begin{aligned} \frac{\partial D_\Sigma}{\partial\theta} &= D\sin 2\theta\frac{\frac{1}{\tilde{b}}+\frac{1}{\tilde{c}}}{1+\frac{1}{\tilde{b}}+\frac{1}{\tilde{c}}} \ge 0, \\ \frac{\partial D_\Sigma}{\partial\gamma} &= D\sin 2\gamma\frac{1+\frac{1}{\tilde{b}}}{1+\frac{1}{\tilde{b}}+\frac{1}{\tilde{c}}} \ge 0. \end{aligned} \tag{27}$$

Evidently, derivatives (27) cannot be nullified simultaneously. Therefore, the function $D_\Sigma(\theta, \gamma)$ has no minimum inside the region of the parameter's definition; this minimum lies on the boundary of the definition region $\Gamma(\theta, \gamma) = \{0 \le \theta \le \pi/2, \pi/2 - \theta \le \gamma \le \pi/2\}$. When $\theta = 0$, we have $\gamma = \text{const} = \pi/2$; therefore, along the boundary $\theta = 0$, from Eq. (26),

$$\min D_\Sigma(0, \gamma) = D\left(\frac{1+\frac{1}{\tilde{b}}}{1+\frac{1}{\tilde{b}}+\frac{1}{\tilde{c}}}\right). \tag{28}$$

In the same way, along the boundary $\gamma = 0$, we have $\theta = \pi/2$; then, from (26),

$$\min D_\Sigma = D\left(\frac{\frac{1}{\tilde{b}}+\frac{1}{\tilde{c}}}{1+\frac{1}{\tilde{b}}+\frac{1}{\tilde{c}}}\right). \tag{29}$$

From a comparison of (28) and (29), the minimal generalized diffusion coefficient is specified by (28) when a parallelotope lies on plane (a, b).

CONCLUSIONS

We have derived Eq. (16) for intergrain diffusion with account for the grain surface topology. This diffusion equation includes the specific grain surface and terms of the topological tensor. The generalized intergrain diffusion tensor depends on the surface grain topology. Changing topological tensor terms, one can control diffusion in technological purposes. In the above particular case where grain surfaces are fitted by parallelotope surfaces, the generalized diffusion coefficient can be changed by two relative quantities: the parallelotope width and height and its arrangement with respect to the diffusion direction.

It is noteworthy that diffusion is affected by the specific surface area gradient and not by the specific surface area itself. This becomes clear if the specific surface area in Eq. (16) is set constant and the left-hand and right-hand sides of this equation are divided by the aforementioned constant specific area.

We suggest the following scheme for provisional analysis of intergrain diffusion in practical applications with the use of Eq. (18) for the generalized diffusion tensor: (1) set the approximation of the grain surface; and (2) calculate, on the basis of this approximation, the specific surface area and terms of the topological tensor and obtain the expression for the generalized diffusion coefficient. This scheme was considered above for the model fitting grain surfaces by parallelotope surfaces for the case of a one-dimensional diffusion equation.

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