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1D to 3D diffusion-reaction kinetics of defects in crystals

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Microstructural features evolving in crystalline solids from diffusion-reaction kinetics of mobile components depend crucially on the dimension of the underlying diffusion process which is commonly assumed to be three-dimensional (3D). In metals, irradiation-induced displacement cascades produce clusters of self-interstitials performing 1D diffusion. Changes between equivalent 1D diffusion paths and transversal diffusion result in diffusion-reaction kinetics between one and three dimensions. An analytical approach suggests a single-variable function (master curve) interpolating between the 1D and 3D limiting cases. The analytical result is fully confirmed by kinetic Monte Carlo simulations.

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The diffusion of mobile defects, such as substitutional or interstitial impurity atoms and thermally or irradiation-induced vacancies and self-interstitial atoms (SIA's), and their reaction with other mobile or immobile defects, play a crucial role in the microstructural evolution of crystalline materials and the associated material properties. A classical example is the precipitation of mobile substitutional impurities by the nucleation of the second-phase particles and their subsequent ''Ostwald ripening'' by the diffusional transfer of impurities from small to large particles.

The characteristic spatial length scale in a microstructure resulting from diffusion-reaction kinetics of mobile defects is defined by their mean diffusion range, which itself is determined by the average size of and distance between the relevant reaction partners (precipitates, bubbles, voids). For normal three-dimensional (3D) diffusion, this length scale is in most cases not substantially larger than the average distance between the relevant immobile reaction partners.[1–3] Consequently, the microstructure appears homogeneous on length scales larger than the distance between those components.

Many experimental studies of microstructures evolving in metals during irradiation with energetic ions or neutrons have revealed strikingly heterogeneous and segregated accumulations of vacancies and SIA's.[4] The accumulation of vacancies in voids, for instance, has been found to be considerably enhanced in several-micrometer-wide regions adjacent to grain boundaries. On the other hand, SIA-type dislocation loops have been observed to accumulate in regions close to dislocations separated by several micrometers, while vacancies accumulate in between at very high rates. The characteristic length scales of several micrometers of such microstructures can be more than one order-of-magnitude larger than expected in any type of 3D diffusion-reaction kinetics.

These surprising features have been explained by the production of thermally stable SIA clusters within displacement cascades [the basic ingredient of the so-called ''production bias model,'' [5]] and the far-ranging 1D diffusion of those SIA clusters, which form glissile dislocation loops, along close-packed directions of the crystal lattice, until they react with other defect components.[3,6–8] The large mean 1D diffusion range, corresponding to the mean free path in collision physics, has indeed been shown to correlate well with the spatial scales of the observed heterogeneous microstructures.[6] We add here, that the surprisingly large range of SIA-type defects, frequently observed in ion implantation to exceed the ion and primary damage ranges by up to a factor of 5,[9] is also most likely due to the far-ranging 1D transport of cascade-induced SIA clusters. It is interesting in the present context that 1D diffusion of adatom clusters is also occurring on metal surfaces.[10]

The idea of 1D diffusion of SIA clusters has been confirmed by many molecular-dynamics simulations[11–14] which show, in addition, changes between crystallographically equivalent 1D directions.[11,12] There are, in fact, experimental findings, such as the saturation of void growth in void lattices, which can be rationalized in terms of 1D diffusion of SIA clusters only if direction changes in the 1D diffusion and/or some transversal diffusion (for instance, by random self-climb of small dislocation loops[3,7]) is included.[8]

Direction changes and transversal diffusion disturb the pure 1D diffusion-reaction kinetics of SIA clusters. Increasing rates of these processes are expected to induce a continuous transition from 1D to 3D kinetics. For 1D diffusion with direction changes, the character of the defect reaction kinetics depends on the relationship between the following three main types of length scales involved.[8,3]

(i) the mean 1D diffusion length, $l_{\mathrm{ch}}=\sqrt{2D_{\mathrm{lo}}\tau_{\mathrm{ch}}}$, covered during the time between two direction changes, τ_{ch}, in a sink-free virtual crystal, where D_{lo} is the 1D (longitudinal) diffusion coefficient;

(ii) the mean 1D diffusion range in a certain microstructure, given, for instance, by $\lambda_1=(\sigma N)^{-1}$ for a monodisperse random distribution of sinks of absorption cross section σ and number density N; and

(iii) the linear dimension of the sinks, for instance, the absorption radius R of spherical sinks.

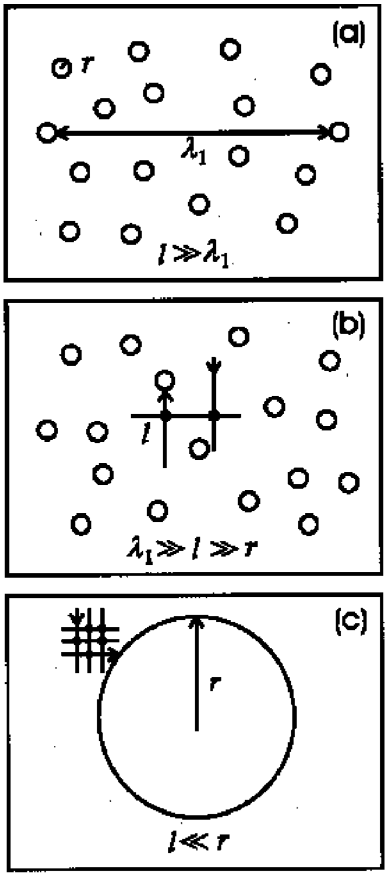

FIG. 1. Illustration of the three characteristic cases in the reaction kinetics of a piecewise 1D diffusing defect with an immobile sink; (a) correlated 1D, (b) uncorrelated 1D, and (c) 3D.

The three physically meaningful relationships between these length scales define three characteristic cases in the reaction kinetics as illustrated in Fig. 1:

(i) The pure (correlated) 1D case defined by $l_{\mathrm{ch}} \gg \lambda_1$ [Fig. 1(a)]. In this case, any given straight 1D diffusion line is terminated by two unambiguously defined individual sinks, which is associated with a two-sink correlation in the reaction kinetics[2,3,6,7] (see below).

(ii) An intermediate case defined by $\lambda_1 \gg l_{\mathrm{ch}} \gg R$ [Fig. 1(b)]. The correlation between sinks characteristic for the pure 1D case is obviously broken by direction changes, but an important feature of the 1D case, the dependence of the kinetics on absorption cross sections rather than linear dimensions of the sinks, is maintained. Therefore, we call this case ‘‘uncorrelated 1D reaction kinetics’’ (see below).

(iii) The well-known 3D case defined by $l_{\mathrm{ch}} \ll R$ [Fig. 1(c)].

Reaction kinetics of defects performing anisotropic diffusion without changes in the direction of fastest diffusion was discussed already some time ago.[2] A treatment of 1D reaction kinetics including the transition between cases (i) and (ii) as illustrated in Figs. 1(a) and 1(b), respectively, has been presented only recently.[15] These cases were also studied by kinetic Monte Carlo (KMC) simulations.[16] A continuous transition from 1D to 3D reaction kinetics induced by direction changes as illustrated in Figs. 1(a)–1(c) has not been treated so far, however.

In the following, we present a short derivation of an expression for the sink strength (or absorption rate) of 1D diffusing defects interrupted by direction changes (cases i and ii) and consider the physical meaning of terms in this expression to include transversal diffusion and the limiting case of 3D case. The resulting generalized expression is then tested by KMC simulations.

In order to introduce the relevant physical quantities, we consider the spatial evolution of the concentration c of a certain type of mobile defects produced randomly in space and time at a production rate P, and diffusing (in 3D) with diffusion coefficient D until getting absorbed by randomly distributed immobile sinks of strength k^2 (sink-dominated defect annihilation). In the mean-field approximation, suited for treating the global reaction kinetics, this problem is described by the linear diffusion-reaction equation[1]

$$\partial c/\partial t = P + D\Delta c - Dck^2. \tag{1}$$

The characteristic spatial and temporal scales defined by (exponential solutions of) Eq. (1) are the mean diffusion range $\lambda = k^{-1}$ and the mean lifetime $\tau_1 = 1/Dk^2$, of the defects, respectively. Both are controlled by the sink strength k^2, which is to be determined by some appropriate procedure.[1] For strictly 1D diffusion, D in Eq. (1) may be substituted by the (longitudinal) 1D diffusion coefficient D_{lo}, the Laplacian Δ by $\partial^2 c/\partial x^2$ for defects diffusing in the x direction, and k^2 by an appropriate 1D sink strength. For the general 1D to 3D diffusion-reaction kinetics considered in the following, we will, however, keep the form of Eq. (1), and particularly the corresponding definition of the sink strength k^2, taking into account that, on a very large spatial scale of a sink-free virtual crystal, even almost perfect 1D diffusion would be effectively 3D with a 3D diffusion coefficient $D = D_{\mathrm{lo}}/3$.

In treating the problem of 1D to 3D diffusion-reaction kinetics, we first consider 1D defect diffusion interrupted by direction changes, assuming $l_{\mathrm{ch}} \gg R$ (cases i and ii) and ignoring transversal diffusion. To derive an expression for the sink strength k^2, we assume a steady state in the following self-consistent embedding procedure. We consider one individual sink of type i with cross section σ_i embedded into a homogeneous background of randomly distributed sinks of total strength k^2, which is to be defined by the rate of absorption of the defects by all individual sinks.

As long as $l_{\mathrm{ch}} \gg R_i$, the considered sink defines $2n$ defect drainage cylinders (two for each direction) in which defects diffusing in n crystallographically equivalent 1D directions flow towards the sink ($n = 6$ for fcc crystals). Within a certain drainage cylinder only the concentration of the corresponding defect configuration is significantly affected (reduced) by the sink whereas the concentrations of the other defect configurations are virtually unaffected under this condition. Furthermore, the average time for a defect to leave its drainage cylinder after a direction change is negligibly small compared to τ_{ch}.

Using these approximations, we may modify the steady-state version of Eq. (1) for the local concentration $c_\mu(x)$ of defects of configuration μ produced at a constant partial production rate P_μ and diffusing in the direction μ along the corresponding drainage cylinder of the individual sink considered (chosen to be oriented in the direction of the x coordinate):

$$P_\mu = -3D\partial^2 c_\mu/\partial x^2 + Dk^2(c_\mu + \langle c_\mu\rangle)/2 + (c_\mu - \langle c_\mu\rangle)/\tau_{\mathrm{ch}}, \tag{2}$$

where $\langle c_\mu\rangle = c_\mu(x\to\infty) = P_\mu/Dk^2$ is the average defect concentration far away from the sink considered. The three terms at the right-hand side of Eq. (2) describe the diffusion of defects μ along the drainage cylinder (where $D_{\mathrm{lo}} = 3D$ has been used), their absorption by two types of sides of sinks in the background, and their loss and gain by direction changes, respectively. In the second term, the orientation of the background sinks with respect to the individual sink considered must be taken into account. Thus, the presence of this sink only affects the absorption of defects by the sides of the background sinks turned towards it but not by the sides turned away from it. Accordingly, the defect concentration has to be split into local and distant parts $c_\mu/2$ and $\langle c_\mu\rangle/2$, respectively.

The solution of Eq. (2), subject to the boundary conditions $c_\mu(x=0)=0$ and $c_\mu(x\to\infty)\to\langle c_\mu\rangle$, is

$$c_\mu = (P_\mu/Dk^2)[1-\exp(-k'x)], \tag{3}$$

with

$$3k'^2 = k^2/2 + 6/l_{\mathrm{ch}}^2. \tag{4}$$

The flux density defined by Eq. (3), $j_\mu = -D_{\mathrm{lo}}\partial c_\mu/\partial x$, yields for the two-sided total flux I_i to a sink of type i

$$I_i = 2|j(x=0)|\sigma_i = 6(P_\mu/k^2)k'\sigma_i. \tag{5}$$

In the steady state, the self-consistency condition consists of equating the total flux to all individual sinks [Eq. (5)], multiplied by the number density of sinks of types i, N_i, and summed up over i, with the production rate, which yields

$$k^2 = 6k'\Sigma_i\kappa_i,$$

with

$$\kappa_i = \lambda_i^{-1} = \sigma_i N_i. \tag{6}$$

The form of Eq. (6) suggests considering $k_i^2 = 6k'\kappa_i$ as the partial sink strengths of sinks of type i. Equations (4) and (6) yield quadratic equations for k^2 and k', the solutions of which result in an expression for the partial sink strengths

$$k_i^2 = 3\kappa_i\kappa[1+\sqrt{(1+8/\kappa^2 l_{\mathrm{ch}}^2)}]. \tag{7}$$

Expression (7) for k_i^2 represents a very good approximation to a corresponding expression in form of an integral obtained by considering average defect lifetimes in a random distribution of sinks.[15]

In Eq. (7), twice the reciprocal of the function in the square brackets may be considered as a measure of the degree of diffusional correlation between two neighboring sinks characteristic of the 1D diffusion-reaction kinetics. This correlation function decreases with decreasing l_{ch} from 1 for $l_{\mathrm{ch}}^2\to\infty$ and to 0 for $l_{\mathrm{ch}}\to 0$. Note that this function depends, via κ^2, only on the total sink structure but not on its individual components.

In the two limiting cases of correlated (pure) and uncorrelated 1D diffusion, respectively, Eq. (7) simplifies to

$$k_i^2 \to k_{(1)i}^2 = 6\kappa_i\kappa \quad \text{for } l_{\mathrm{ch}} \gg \lambda, \tag{8a}$$

$$k_i^2 \to 6\sqrt{2}\kappa_i/l_{\mathrm{ch}} \quad \text{for } \lambda \gg l_{\mathrm{ch}} \gg R_i. \tag{8b}$$

Due to the two-sink correlation, the limiting case $k_{(1)i}^2$ for correlated 1D diffusion is quadratic in the sink density, establishing, together with the concentration of the mobile defects, reaction kinetics of third order.[2,3,6,7] The increase of k_i^2 with decreasing l_{ch} for $\lambda \gg l_{\mathrm{ch}} \gg R_i$ reflects the increase in the search-and-find efficiency with increasing frequency of direction changes in the 1D diffusion of the defects.

Even though Eq. (7) is restricted to a weak disturbance of the pure 1D diffusion by direction changes, $l_{\mathrm{ch}} \gg R_i$, it provides a basis for including transversal diffusion and the transition to the limiting case of 3D diffusion by direction changes reached when $l_{\mathrm{ch}} \ll R_i$. This may be done by generalizing the time of 1D diffusion along a certain drainage cylinder τ_{ch}, contained in Eqs. (2) and (7). Anisotropic diffusion without changes in the direction of fastest diffusion has been treated previously.[2] We focus therefore here on the transition to 3D diffusion by direction changes.

In this case, we interpret τ_{ch} as the average time of a defect for staying in a certain drainage cylinder. When R_i is no longer negligible compared to l_{ch}, the average time of a defect for entering and leaving the drainage cylinder before and after the period of 1D diffusion along it, respectively, $\tau_{\mathrm{lo}} \propto R_i^2/D_{\mathrm{lo}}$, would have to be included in the average stay time in addition to τ_{ch}. This suggests that τ_{ch} in Eq. (7) should be substituted by $(\tau_{\mathrm{ch}} + \tau_{\mathrm{lo}})$. In the corresponding generalization of Eq. (7), a numerical factor of the order of 1 in $\tau_{\mathrm{lo}} \propto R_i^2/D_{\mathrm{lo}}$ is to be determined such that the partial sink strength becomes exact, i.e., equal to $k_{(3)i}^2$, in the limiting case of 3D diffusion $l_{\mathrm{ch}}\to 0$, and low sink volume fraction defined as $k_{(1)i}^4/k_{(3)i}^4 \to 0$. Using in $\tau_{\mathrm{lo}} \propto R_i^2/D_{\mathrm{lo}}$ that $R_i^2 \propto \kappa_i^2/k_{(3)i}^4$, we find that this requirement is fulfilled by setting $\tau_{\mathrm{lo}} = 4\kappa_i^2/(D_{\mathrm{lo}}k_{(3)i}^4)$. The resulting generalized version of Eq. (7) may then be written as a single variable function in the form

$$y = 0.5\{1+\sqrt{(1+4/x^2)}\} \tag{9a}$$

with

$$y = k_i^2/k_{(1)i}^2, \quad x^2 = (l_{\mathrm{ch}}^2 k_{(1)}^2/12 + k_{(1)i}^4/k_{(3)i}^4). \tag{9b}$$

This function, plotted in Fig. 2, represents a master curve for the dependence of the sink strength on the three main spatial scales l_{ch}, λ_1, and R_i involved.

Transversal diffusion may be included in a similar way, except that it is the total *rate* of gain and loss of defects diffusing in a drainage cylinder to which the rates of direction change and transversal diffusion, i.e., the corresponding *reciprocal times*, sum up in this case.

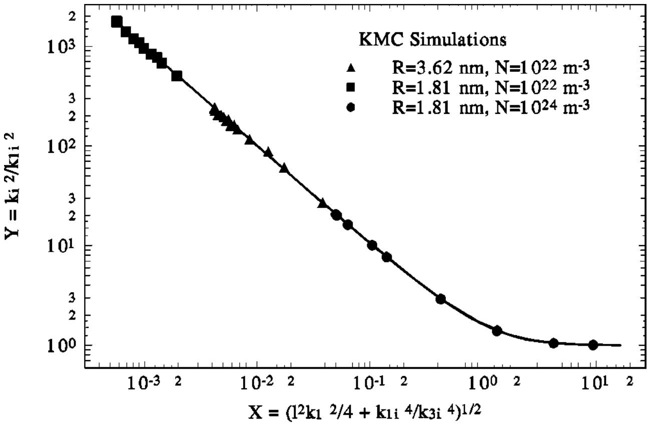

FIG. 2. ‘‘Master curve’’ interpolating between the sink strengths for the 1D and 3D limiting cases (solid line) and KMC simulation data for $N=10^{22}$ m^{-3} and various values of R and l_{ch} (symbols). For each value of R the different points are the results for values of l_{ch} in the range corresponding to $n_{\mathrm{ch}}=1-10^6$.

Kinetic Monte Carlo simulations were performed to study 1D to 3D defect diffusion-reaction kinetics in a simple model system consisting of a fcc lattice of 1-μm^3 cubic volume (lattice parameter of Cu) in which defects migrating along close-packed directions of the lattice are allowed to change from one to another direction until they are absorbed by one of the randomly arranged spherical sinks of capture radius R and number density N. These sinks did not change size or position upon absorbing defects. For given R and N, thousands of defects traversed the computational cell, one at a time, each hopping from lattice site to lattice site along a randomly chosen close-packed direction in a 1D random walk, changing to another randomly chosen direction after a fixed number of hops n_{ch}. Periodic boundary conditions were imposed. The average lifetime of the defects (total number of jumps before absorption) was used to determine the sink strength as a function of R, N, and l_{ch} through the relation

$$k^2=2/a\langle j\rangle, \tag{10}$$

where a is the jump distance along the [110] direction, and $\langle j\rangle$ is the average number of jumps per defects.

To compare the simulations with Eq. (9), the discreteness of the lattice must be accounted for. As the value of l_{ch} approaches the 3D limit consisting of random hops to nearest-neighbor sites, its path is still a series of hops along close-packed directions, even though consisting of only one hop between direction changes in this limit. Thus, we must use the value of the 3D limit for the sink strength determined from the KMC simulations when comparing the discrete simulations with Eq. (9). Figure 2 shows such a comparison. Note that the simulation data include the intermediate case of the ‘‘uncorrelated 1D’’ and 3D limits. Perfect agreement, within the accuracy of the simulations, is found between the simulations and our ‘‘master curve.’’

In view of this encouraging agreement, we recommend the use of our analytical description of 1D to 3D diffusion-reaction kinetics of defects generated in displacement cascades as the basis for future modeling microstructures evolving under cascade damage conditions.

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