Nonlinear diffusion of interstitial atoms

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A nonlinear kinetic discrete model for interstitial diffusion in a nonuniform system is presented, based on Martin's deterministic model and Hillert's sublattice theory, where the diffusion coefficient of interstitial atoms strongly depends on their local concentration. The nonlinear diffusion of interstitial atoms is characterized by the concentration-dependent correlation coefficient γ and the relaxation time τ, which are determined by the pair interaction energies between interstitial atoms and between interstitial atoms and matrix atoms, respectively. This model exceeds the range of validity of the traditional Fick's law, and allows of an extension of Fick's law to diffusion on the nanoscale.

For a nonuniform system having a spatial variation in one of its intensive scalar properties, such as composition or density, Cahn and Hilliard[1] derived a general equation for the free energy of the system in terms of a regular solution model. Subsequently, Hillert[2] and Cahn[3] introduced a model for interdiffusion in a nonuniform system where the contribution of variation in composition to the chemical potential is taken into account. In order to evaluate the atomic mobility in Cahn's diffusion model, Martin[4] proposed a deterministic model for one-dimensional interdiffusion using the free energy for a nonuniform system of Cahn and Hilliard,[1] finding the interdiffusion flux of substitutional atoms to be dependent on their local equilibrium composition and composition inhomogeneity. The diffusion behavior of nanostructured materials has received significant attention recently due to the essential spatiotemporal stability achievable in these materials.[5] Beke and co-workers[6,7] proved successfully that nonlinear interdiffusion occurs in binary substitutional solid solutions, using Martin's deterministic model, discovering that the substitutional interdiffusion on the nanoscale deviates from that described by the traditional Fick's law. Interstitial diffusion is another mechanism of diffusion, the diffusivities of which are often many orders of magnitude greater than those of substitutional diffusion. Although the free energy of an interstitial solid solution can be calculated by the classical regular solution model on the condition that a sublattice theory introduced by Hillert and Staffansson[8] is used to deal with the interstitial solid solution, determination of the free energy of an interstitial solid solution for a nonuniform system is not fully clear, so that the diffusion of interstitial atoms in a nonuniform system is not understood.[9] In this Brief Report, the diffusion of interstitial atoms in a nonuniform system is described by Martin's deterministic model using the free energy of the nonuniform interstitial solid solution. Hillert's sublattice theory is used to separate the interstitial solid solution into two interpenetrating sublattices: the interstitial sublattice and the matrix sublattice. The interaction between the interstitial and matrix sublattices is also considered to evaluate the atomic mobility of interstitial atoms in the nonuniform system. A nonlinear kinetic discrete model for interstitial diffusion is presented to characterize the nonlinear diffusion of interstitial atoms.

The interstitial solid solution is composed of a base element A, any substitutional dissolved element B, and an interstitial dissolved element I. The diffusion of interstitial atoms is supposed to be interdiffusion of interstitial atoms I and interstices V, which can be regarded as an additional component of the interstitial sublattice. The matrix sublattice is completely filled by the base elements A and B, the diffusion of which does not take place. The concentration of interstitial atoms in the interstitial solid solution is given by $c(x) = c_n/(c_n + \beta)$ with $x = (n-1)a$, where the atomic fraction of interstitial atoms c_n is the ratio of the number of interstitial sites and interstitial atoms in the nth interstitial lattice plane, β is the number of matrix atoms belonging to one interstitial site, and a is the interplanar distance of interstitial lattice planes. The time derivatives of c_n in the nonlinear kinetic discrete model can be given by

$$\frac{dc_n}{dt} = J_{n-1,n} - J_{n,n+1}, \tag{1}$$

where $J_{n,n+1}$ is the net flux of interstitial atoms from interstitial lattice plane n to $(n+1)$,

$$J_{n,n+1} = c_n[z_v(1-c_{n+1})]\Gamma_{n,n+1} - c_{n+1}[z_v(1-c_n)]\Gamma_{n+1,n}, \tag{2}$$

where z_v is the vertical coordination number of interstitial atoms, $\Gamma_{n,n+1}$ is the jump frequency of interstitial atoms, which has an Arrhenius-type temperature dependence at a general diffusion temperature, $\Gamma_{n,n+1} = \nu \exp(-E_{n,n+1}/kT)$, where ν is the attempt frequency of interstitial atoms, k and T are the Boltzmann constant and the temperature, respectively, and $E_{n,n+1}$ is the activation energy of diffusion for interstitial atoms,

$$\begin{aligned} E_{n,n+1} = {} & E^0 - Z(V_{IV} + V_{VV}) - E_{IM} \\ & - [z_v(c_n + c_{n+2}) + z_l c_{n+1}](V_{IV} - V_{VV}) \\ & + [z_v(c_{n-1} + c_{n+1}) + z_l c_n](V_{IV} - V_{II}), \end{aligned} \tag{3}$$

where E^0 is the saddle point energy, z_l is the lateral coordination number of interstitial atoms, and the coordination number of the interstitial atoms is $Z = 2z_v + z_l$. V_{II}, V_{IV}, and V_{VV} are the pair interaction energies between interstitial atoms I and interstices V. E_{IM} is the interaction energy between interstitial atoms and matrix atoms given by the pair interaction energies. According to Eqs. (2) and (3), the dif-

fusion coefficients $D_{n,n+1}$ and $D_{n+1,n}$ of interstitial atoms between interstitial lattice planes can be expressed as

$$D_{n,n+1} = z_v a^2 \Gamma_{n,n+1},$$

$$D_{n+1,n} = z_v a^2 \Gamma_{n+1,n}. \tag{4}$$

It is noted that $D_{n,n+1}$ and $D_{n+1,n}$ are functions of the atomic fractions of interstitial atoms in the interstitial lattice planes $(n-1)$ to $(n+2)$, which are strongly dependent on the local concentration of interstitial atoms in comparison with the diffusion in the traditional Fick's law.

The concentration-dependent correlation coefficient γ is defined to describe the degree of concentration dependence of the diffusion coefficient of interstitial atoms, which is expressed by the natural logarithm of the ratio of the diffusion coefficients of interstitial atoms with the atomic fractions of $c_n=0$ (D^0) and $c_n=1$ (D^1) in the interstitial sublattice. γ can be expressed as

$$\gamma = \ln\left(\frac{D^0}{D^1}\right) = -\frac{Z(V_{II} - V_{VV})}{kT}. \tag{5}$$

The relaxation time τ is defined to describe the diffusion rate of interstitial atoms in the interstitial solid solution, which is a constant independent of the concentration of interstitial atoms,

$$\tau = \nu^{-1} \exp\left(\frac{E^0 - Z(V_{IV} + V_{VV}) - E_{IM}}{kT}\right). \tag{6}$$

For a constant zero of V_{VV} in a given crystal structure at a certain temperature, γ is inversely proportional to V_{II}. The interaction energy E_{IM} determines the relaxation time τ, whereas it has no effect on the concentration profile of interstitial atoms.

Keeping the atomic fraction of interstitial atoms in the Taylor expansion and ignoring the second- and higher-order terms, $c_n - c_{n+1} = -a \partial c / \partial x$, $c_n + c_{n+1} = 2c$, $c_n c_{n+1} = c^2$, Eq. (2) can be rewritten as

$$J_{n,n+1} = -\frac{D^i}{a} \frac{\partial c}{\partial x}, \tag{7}$$

where D^i is the intrinsic diffusion coefficient, $D^i = z_v a^2 \Gamma \theta$, $\Gamma = \nu \exp\{-[E^0 - Z(V_{IV}+V_{VV}) - E_{IM} - \alpha]/kT\}$ and $\alpha = [cZ + (z_v + Z/4)a^2 \partial^2 c/\partial x^2](V_{II} - V_{VV})$, θ is the thermodynamic factor $\theta = 1 - 2ZVc(1-c)/kT$, and $V = V_{IV} - (V_{II} + V_{VV})/2$. In the regular solution approximation, the nonlinear kinetic discrete model for interstitial diffusion can be transformed into the traditional Fick's first law, in which the intrinsic diffusion coefficient D^i can also be related to the local concentration.

A numerical method was used to calculate the diffusion behavior of interstitial atoms in the interstitial solid solution. In order to investigate the effect of the concentration-dependent correlation coefficient γ and the relaxation time τ on the nonlinear diffusion of interstitial atoms, the initial condition of the interstitial solid solution was that a surface layer composed of eight interstitial lattice planes filled with the interstitial atoms is located at the top of the semi-infinite substrate for a face-centered cubic structure of element A,
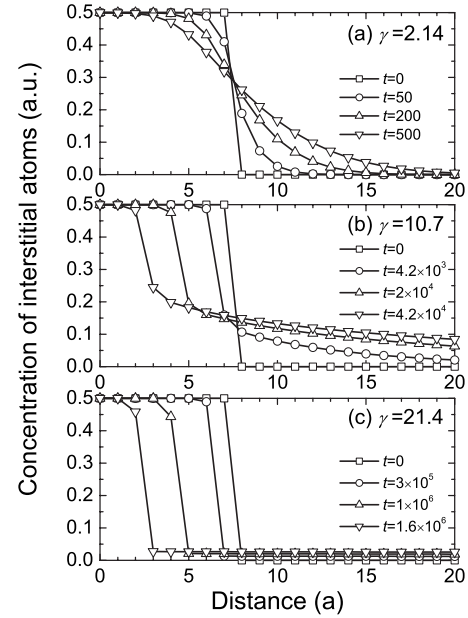

FIG. 1. Concentration evolution of interstitial atoms in an interstitial solid solution as a function of diffusion time t for the concentration-dependent correlation coefficient $\gamma = 2.14$, 10.7, and 21.4 as V_{II} changes from -0.01 to -0.05 to -0.10 eV at the temperature of 650 K.

with no intermixing at the interface. The diffusion direction of interstitial atoms was chosen as the closest-packed direction of [111], i.e., $z_l = 6$ and $z_v = 3$. The concentration evolution of interstitial atoms in the interstitial solid solution was recorded as a function of diffusion time t with a time step $\Delta t = 10^{-2} \tau$.

Figure 1 shows the concentration evolution of interstitial atoms in the interstitial solid solution as a function of diffusion time t for the concentration-dependent correlation coefficient $\gamma = 2.14$, 10.7, and 21.4 as V_{II} is changed from -0.01 to -0.05 to -0.10 eV at the temperature of 650 K. For $\gamma = 2.14$, the concentration gradient of interstitial atoms in the diffusion direction decreased gradually during diffusion. The interface between the surface layer and the substrate became broadened from the thickness of one interstitial lattice plane (a) at $t=0$ to $7a$ at $t=50$, $13a$ at $t=200$, and $19a$ at $t=500$ [Fig. 1(a)]. When γ increased to 10.7, the concentration gradient of interstitial atoms had a break at the interface with a gradually decreasing concentration of interstitial atoms in the substrate. The interface shifted toward the surface layer and thinned to about $4a$ [Fig. 1(b)]. For larger $\gamma = 21.4$, the concentration profile of interstitial atoms on both sides of the surface layer and substrate was practically flat at concentrations of 0.5 and about zero, respectively, during diffusion. The thickness of the interface decreased further to about one interstitial lattice plane, as sharp as it was at $t=0$, and the interface shifted toward the surface layer during diffusion [Fig. 1(c)].

Furthermore, in order to investigate the effect of interaction energy E_{IM} on the diffusion behavior of the interstitial atoms, an interstitial solid solution with three different compositions is considered: composed of (1) only A; (2) A with a
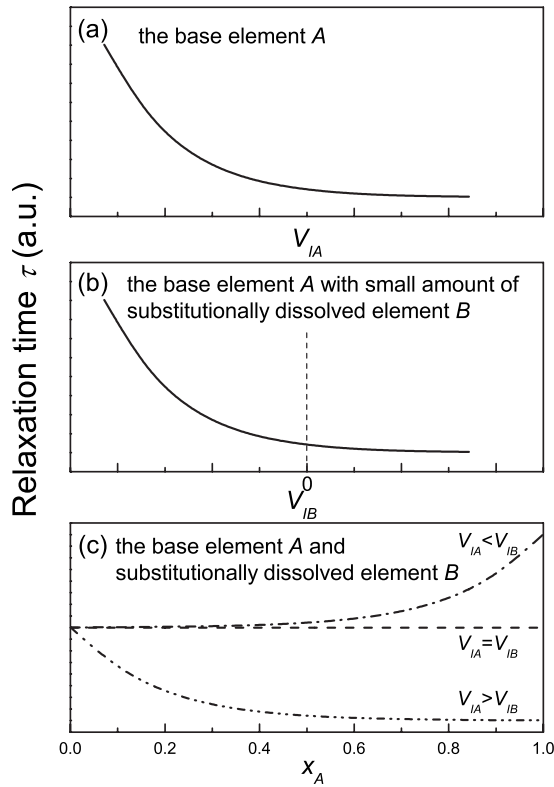
FIG. 2. Relationship between the relaxation time τ and the pair interaction energies between interstitial atoms and matrix atoms for three different compositions in an interstitial solid solution.

small amount of B; (3) A and B. The relaxation time τ can be expressed as

$$\tau_1 = \upsilon^{-1} \exp\{[E^0 - Z(V_{IV} + V_{VV}) - Z_M V_{IA}]/kT\},$$

$$\tau_2 = \upsilon^{-1} \exp\{[E^0 - Z(V_{IV} + V_{VV}) - (Z_M V_{IA} + x_B V_{IB})]/kT\}$$
$$(x_B \ll 1),$$

$$\tau_3 = \upsilon^{-1} \exp\{[E^0 - Z(V_{IV} + V_{VV}) - Z_M(x_A V_{IA} + x_B V_{IB})]/kT\}$$
$$(x_A + x_B = 1), \tag{8}$$

where Z_M is the number of nearest matrix atoms of one interstitial site, V_{IA} and V_{IB} are the nearest pair interaction energies between interstitial atoms I and matrix atoms A and B, and x_A and x_B are the atomic fractions of A and B in the matrix sublattice. Figure 2 shows the relationship between the relaxation time τ and the pair interaction energies between interstitial atoms and matrix atoms for three different compositions in the interstitial solid solution. For the interstitial solid solution composed of A, τ decreased with increasing V_{IA} [Fig. 2(a)]. When B was added to the interstitial solid solution, τ increased for $V_{IB} < 0$ and decreased for $V_{IB} > 0$ for a fixed V_{IA} in the dilute solid solution [Fig. 2(b)]. As a large amount of B dissolved, τ decreased as x_A increased for $V_{IA} > V_{IB}$; while τ increased when x_A increased for $V_{IA} < V_{IB}$; a change of x_A and x_B has no effect on τ for $V_{IA} = V_{IB}$ [Fig. 2(c)].

The diffusion of interstitial atoms in the interstitial solid solution described by the concentration-dependent correlation coefficient γ and the relaxation time τ, i.e., the concentration profile of interstitial atoms characterized by γ and the diffusion rate of interstitial atoms by τ, exceeds the range of validity of the traditional Fick's law. In addition, compared with the traditional Fick's law, the only parameters of the pair interaction energies between components are necessary in the nonlinear kinetic discrete model to characterize the nonlinear diffusion of interstitial atoms in the interstitial solid solution. Even though the diffusion coefficient is relative to the local concentration of atoms in the traditional Fick's law, the traditional Fick's law can break down if the diffusion takes place in a nonuniform system, such as substitutional diffusion in nanoscale multilayers.[10]

As the diffusion temperature increases, interstitial diffusion such as self-interstitial diffusion changes to a strongly non-Arrhenius behavior because the activation energy of interstitial atoms is much smaller than the thermal energy.[11] At higher temperature, the diffusion of interstitial atoms is similar to that of a free particle and their diffusion coefficient is proportional to the diffusion temperature, $D = kT/m\nu$, where m is the mass of the interstitial atom. Compared with Eq. (4), the diffusion coefficient of interstitial atoms is a constant at a high temperature independent of the local concentration. Diffusion of interstitial atoms is independent of their pair interaction energies, and is dependent only on their masses. The non-Arrhenius diffusion of interstitial atoms can be regarded as a limiting case of nonlinear diffusion for the concentration-dependent correlation coefficient $\gamma = 0$.

For the $3d$ transition metal carbides MC with the pair interaction energy of carbon V_{CC} varied from -0.02 to -0.1 eV,[12] an indistinct interface in a MC/M nanoscale multilayer can be observed for MC with a larger V_{CC}, while a sharp interface could be distinguished with a smaller V_{CC}. The change of diffusion temperature also contributes to the variation in the characteristics of the interface in nanoscale multilayers. When the annealing temperature was above 450 °C, a less distinct interface between TiN and Ti sublayers was obtained in nanoscale TiN/Ti multilayers.[13] The larger γ of nanostructured materials tends to form sharp interfaces, which is of benefit to the mechanical properties, for example, interface mixing of nanometer crystallines was shown to be harmful to the hardness,[14] while a smaller γ contributes to forming mixing interfaces, which tends to increase the cohesive force between surface layer and substrate, where sharp interfaces may give rise to film failure by cracking at the interface.[15] In addition, choosing appropriate interstitial atoms in a binary alloy could change the relaxation time τ and thus control the diffusion rate of interstitial atoms, with the view of reaching equilibrium quickly or, on the contrary, of freezing a definite nonequilibrium state, to have an influence upon the properties of the interstitial solid solution.[16] It is well known that the addition of V or Cr to Fe inhibits and that of Si, Co, or Ni to Fe accelerates the graphitization of the FeMC alloy, where $M =$ V, Cr, Si, Co, or Ni.[17,18]

In summary, we have built up a nonlinear kinetic discrete model for interstitial diffusion in a nonuniform system based on Martin's deterministic model combined with Hillert's sublattice theory. In the model, the diffusion coefficient of inter-

stitial atoms is strongly dependent on their local concentration. The nonlinear diffusion of interstitial atoms is characterized by the concentration-dependent correlation coefficient γ and the relaxation time τ, which are determined by the pair interaction energies between interstitial atoms and between interstitial atoms and matrix atoms, respectively. The model exceeds the range of validity of the traditional Fick's law, and extends Fick's law to diffusion at the nanoscale. The choice of appropriate interstitial and matrix atoms in a nonuniform system, such as a nanostructured material, could control the properties of the interstitial solid solution through controllable diffusion at a certain diffusion temperature.

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