PHYSICAL REVIEW B **73**, 035426 (2006)

Resolution of the diffusional paradox predicting infinitely fast kinetics on the nanoscale

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(Received 29 April 2005; revised manuscript received 19 October 2005; published 23 January 2006)

In our paper, we offer a natural resolution for a long-standing paradox in diffusion. We show that the growth rate of the diffusion zone (reaction layer) should not go to infinity with decreasing time (as $1/\sqrt{t}$), just because the diffusion permeability of the interface is finite. Expression for the changeover thickness X^* between the linear and parabolic regimes of the interface shift in phase separating binary $A(B)$ systems is derived in the framework of a deterministic atomistic model for diffusion. X^* lies typically between 0.01 and 300 nm, depending on the composition dependence of the diffusion coefficient and the phase separation tendency of the alloy. While in ideal binary alloys with composition independent diffusivity, the deviation from the parabolic law practically cannot be observed, in real systems (where the diffusion coefficient can change several orders of magnitude with the composition), measurable deviations are expected as it was experimentally observed very recently in the Ni/Cu and Au/Ni systems. We also offer an atomistic explanation for the phenomenological interface transfer coefficient K. It measures the finite interface permeability (proportional to the jump frequency across the interface) and thus it controls the shift of the interface at short times (diffusion distances). Although it is almost exclusively accepted in the literature that linear growth kinetics are the result of interface reaction control, our results suggest that the linear or nonparabolic growth of a reaction layer on the nanoscale cannot be automatically interpreted by an interface reaction.

DOI: 10.1103/PhysRevB.73.035426 PACS number(s): 68.35.Fx, 66.30.Pa

I. INTRODUCTION

It is usually supposed that the kinetics of the formation of a diffusion zone is determined by the diffusion coefficients. For example, in the simple classical Darken limit, the growth of the diffusion zone in a binary $A(B)$ system is determined by the interdiffusion coefficient $D=c_BD_A+c_AD_B$, where D_i and c_i denote the intrinsic diffusion coefficients and the atomic fractions, respectively. However, this approach must fail at short times because according to Fick's first law the growth rate of the zone is proportional to $1/\sqrt{t}$ (see, e.g., Refs. 1–4) which means that the zone grows at an infinitively fast rate when the time t goes to 0. In other words, in the expression of the atomic flux, $J=-D\,\mathrm{grad}\,\rho$ (ρ is the density), the gradient is infinite if there is a discontinuity in the density at the beginning (which is the case in typical interdiffusion measurements), and other phenomena must become rate limiting for short distances (times). The same conclusion can be drawn for the growth of a reaction layer during interdiffusion.[2]

Until now, only two rate limiting effects were extensively treated in the literature: the nucleation rate[5,6] and the interface reaction rate control.[1,3] These plausibly led to deviations from the parabolic growth: for example, in the case of interface reaction control, the growth of the reaction layer, and thus the shift of the interface(s), was *linear* with time. It is important to note that the atomistic explanation for the interface reaction control is still missing.[7,8] Since for the understanding of the growth law of a phase, the first step is the proper description of the motion of individual phase boundaries, we will concentrate on this question, into which nucleation problems do not enter.

Computer simulations have shown[9–12] recently that a thin Ni film dissolved into a Cu substrate practically layer-by-layer at short times. Due to the strong composition dependence of the diffusivity, the atomic flux in Ni was practically zero, only the Ni atoms dissolved into the Cu matrix and these atoms diffused away very fast in the Cu matrix. Each Ni atomic plane dissolved subsequently—the dissolution of the next plane began only after the complete dissolution of the previous one—reproducing the same process. The current atomic fraction of Ni atoms in the interface plane i was approximately a periodic function of time and thus the time averaged values of c_i and the rate of the interface shift v (denoted by $\langle c\rangle$ and $\langle v\rangle$, respectively) were constant. Constant $\langle v\rangle$ means a *linear interface shift*, which was also experimentally confirmed during nanoscale dissolution of Ni into Cu single crystalline substrate.[9]

These results indicate that, in this case, the linear kinetics is inherently related to the finite mass transfer across the interface.

In this paper, it will be shown that the finite diffusion permeability of the interface will be a rate limiting process for short distances or times and a numerical estimation for the changeover thickness between the linear and parabolic regimes will also be given.

II. ESTIMATION OF THE CHANGEOVER THICKNESS

A. Basic Equations

In the framework of a discrete, deterministic kinetic model,[13] the net flux of A atoms from plane i to $(i+1)$ is given by

$$J_{i,i+1}=z_v[c_i(1-c_{i+1})\Gamma_{i,i+1}-c_{i+1}(1-c_i)\Gamma_{i+1,i}], \qquad (1)$$

where c_i is the atomic fraction of A atoms in plane i, $\Gamma_{i,i+1}$ is the frequency with which an A atom in plane i exchanges with a B atom in plane $i+1$, and z_v is the vertical coordination number. It is usually assumed that the exchange frequencies have an Arrhenius type temperature dependence

$$\Gamma_{i,i+1} = \Gamma_i \gamma_i \quad \text{and} \quad \Gamma_{i+1,i} = \Gamma_i / \gamma_i$$

with

$$\Gamma_i = \Gamma_0 \exp[\alpha_i / kT] \quad \text{and} \quad \gamma_i = \exp[-\varepsilon_i / kT],$$

where $\Gamma_0 = \nu \exp[-\hat{E}_0 / kT]$, ν denotes the attempt frequency, $\hat{E}_0$ is composition independent and contains the saddle point energy, k is the Boltzmann constant, T is the absolute temperature, and (see also Refs. 9, 10, and 14–16)

$$\alpha_i = [z_v(c_{i-1} + c_{i+1} + c_i + c_{i+2}) + z_l(c_i + c_{i+1})]M$$

as well as

$$\varepsilon_i = [z_v(c_{i-1} + c_{i+1} - c_i - c_{i+2}) + z_l(c_i - c_{i+1})]V.$$

Here V is the regular solid solution parameter,[10] proportional to the heat of mixing and z_l is the lateral coordination number ($Z=2z_v+z_l$). For phase separating systems, $V>0$. The parameter $M=mkT/2Z$ determines the strength of the composition dependence of the transition rates.[17,18] It can be estimated, e.g., from the nearest neighbor pair interaction energies of ij atomic pairs V_{ij} as $M=(V_{AA}-V_{BB})/2$, or can be deduced from the composition dependence of the diffusion coefficients:[17] $D(c)=D(0)\exp(mc)$. For example, m is about 10 and 16 in the Ni-Cu and Mo-V systems, respectively,[11,12,19] which means, e.g., that the diffusion is about 4–5 orders of magnitude faster in the Cu matrix than in the Ni.

B. Form of the Interface Current

According to the results obtained for the dissolution of a Ni thin film into a Cu substrate,[9] the flux J_I across a coherent interface at the very beginning of a dissolution process [i.e., taking $c_{i-2}=c_{i-1}=1$, $c_{i+1}=c_{i+2}=0$; see also Fig. 1(a)] is

$$J_I = J_{i,i+1} = z_v c_i(t) \Gamma_{i,i+1} \cong z_v \langle c \rangle \Gamma_{i,i+1}.$$

In this expression at a bit longer times (and not just at the beginning), we have to take into account that the composition of plane $(i+1)$ is also different from 0 (see Fig. 1). Let us denote this by $c_\beta(=c_{i+1})$. Thus from Eq. (1),

$$J_I = z_v \Gamma_I \gamma_I (1 + \varphi)\Delta c \tag{2a}$$

with

$$\varphi = \frac{c_\beta(1 - \langle c \rangle)}{\Delta c}(1 - 1/\gamma_I^2), \tag{2b}$$

where $\Delta c = \langle c \rangle - c_\beta$. In Γ_I and γ_I, $\alpha_I = [z_v + (z_l + z_v)(\langle c \rangle + c_\beta)]M$ and $\varepsilon_I = [z_v + (z_l - z_v)\Delta c]V$, respectively. Since in all the cases investigated below the values of φ were always between 0 and −0.25, φ has been neglected as compared to 1, which leads to an error of maximum 25% in the following considerations.

In fact, in Eq. (2a), c_β changes slightly with time, which is also related to the following simulation results:[9] after the dissolution of a certain number of layers the transition from linear to parabolic shift started. This also means that with increasing time, J_I decreases slightly.

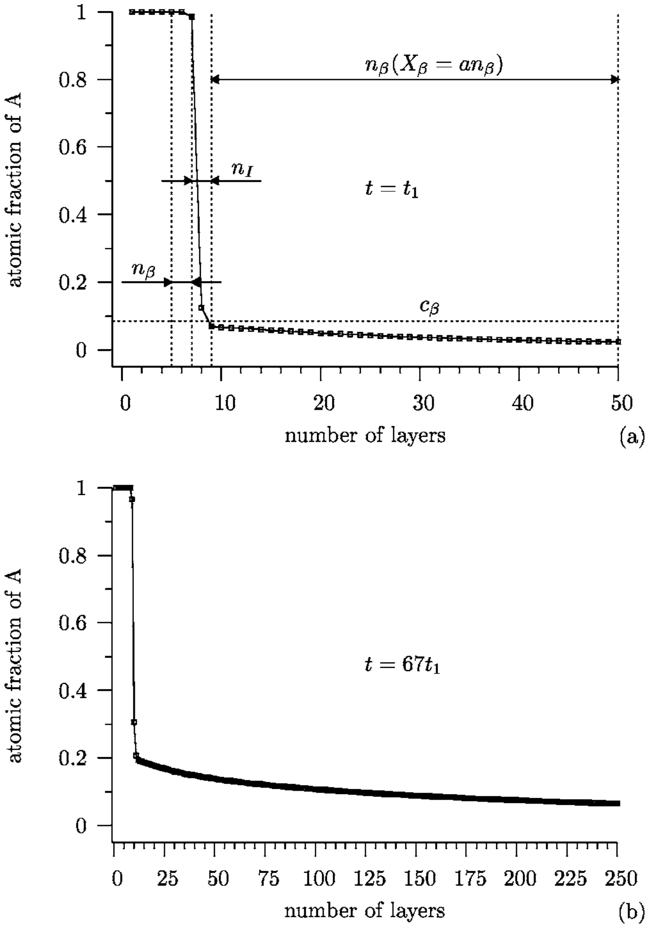

FIG. 1. Calculated composition profiles at $V/kT=0.09\approx 0$ (nearly ideal system) and $m=-16.11$ for two different running times: (a) $t=t_1$ and (b) $t=67t_1$. It can be seen that, because of the large diffusion asymmetry ($|m|$ is large), the upper part of interface remains sharp and shifts. The composition at the kink of the profile (denoted by c_β in the text) slightly increases with time. The division of the composition profile into three regions is illustrated in (a) and the composition of the plane belonging to the "interface" is denoted by c_i in the text.

According to Eqs. (2a) and (2b), for a more refined treatment, an estimation of both the $\langle c \rangle$ and c_β values is necessary. For example, it was obtained from numerical estimations[9] for $V=0$ (ideal system) and $m=-22.3$ (at $T=1000$ K and for $z_v=3$, $z_l=6$) that $\langle c \rangle=0.78$ and it was practically independent of the temperature in the range investigated. Obviously it is generally expected that $\langle c \rangle$ depends on V and m; for $m<0$ (the diffusion in the B-rich phase is faster) and $V=0$, $\langle c \rangle$ lies between 0.5 and 1 (for larger negative m, $\langle c \rangle$ will be larger and closer to unity). Furthermore, as will also be shown later, for large V values, c_β can be taken as the solubility limit, while for very small or negligible values of V, c_β should be estimated from simulations of the composition profile (see Fig. 2).

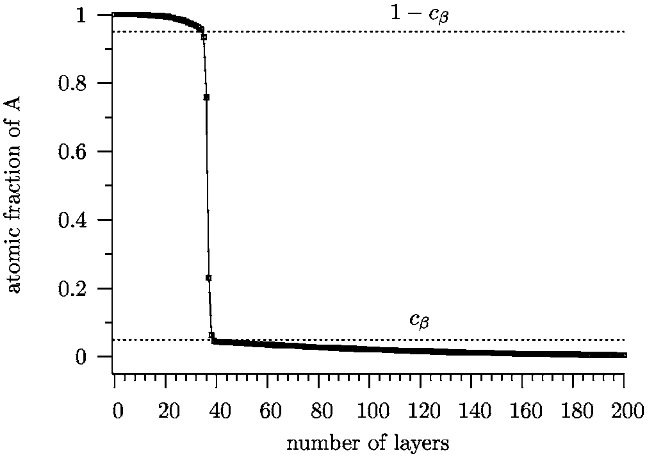

FIG. 2. Calculated composition profile at $V/kT=0.36$ (phase separating system) and $m=-16,11$. Here c_β and $1-c_\beta$ denote the miscibility gap and, similarly as in Fig. 1, the asymmetry of the profile is visible as well.

C. Condition for the Changeover Thickness

On the basis of the above results, we can state the following: for $m<0$, at the beginning, when the composition gradient is very large, the flux in the B-rich phase (β phase) is larger than across the interface ($J_I<J_\beta$). In this stage, J_I controls the dissolution process. During the process, J_β becomes smaller and smaller because the tail of the composition profile in the β phase grows more and more, resulting in the decrease of the gradient of the composition. Although, as was mentioned above, J_I also decreases with increasing time or number of layers dissolved, but J_β decreases much faster. As a result, in a certain moment, J_β becomes smaller than the J_I, and from this point, J_β is the rate limiting. Thus the transition time or thickness must be deduced from the condition

$$J_\beta=J_I, \tag{3}$$

which has to be fulfilled at the interface (see Fig. 3).

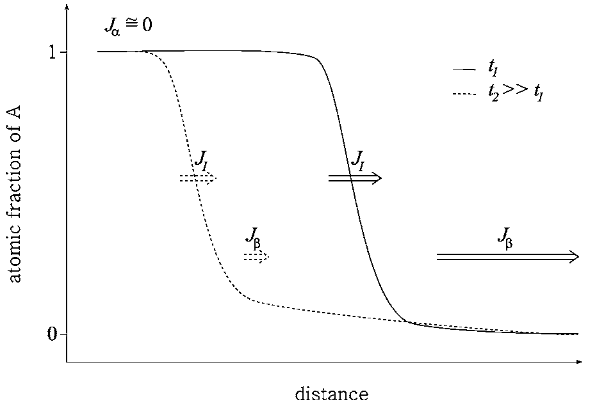

FIG. 3. Scheme of the composition profile and the atomic fluxes in the linear (t_1, solid line) and parabolic ($t_2\gg t_1$, dashed line) kinetic regimes. In the linear regime $J_\beta\gg J_I$, whereas in the parabolic one $J_\beta\ll J_I$. The length of the arrows illustrates the intensity of the fluxes. Note that for large $|m|$, J_α is practically zero as indicated.

Now we look for an appropriate form of the diffusion flux J_β in the long time limit when the composition profiles, except the very narrow interface area, should be flat enough (see Figs. 1 and 2).

For the thickness of the diffusion zone, we can write $X=X_\alpha+X_I+X_\beta=n_\alpha a+n_I a+n_\beta a$, where n_α and n_β are the numbers of atomic planes along which the composition falls in the α and β phases on the left-hand and right-hand side of the interface, respectively. The parameter a is the distance between the neighboring atomic planes in the direction of diffusion and the thickness of the interface is $n_I a$. In cases of large diffusion asymmetry ($|m|$ is large), in the long time limit, $X\cong X_\beta$ can be a good approximation.

Now one can find an expression for J_β from the continuum form of $j_\beta=a\Omega^{-1}J_\beta$ [obtained from Eq. (1), see, e.g., Refs. 9 and 10]: $j_\beta=-\Omega^{-1}D_\beta\,\mathrm{grad}_\beta\, c$, where Ω is the atomic volume and $D_\beta=z_v a^2\Gamma_0\Theta\exp(mc_\beta)$. Θ is the thermodynamic factor[20] for which, in the following, $\Theta\cong 1$ will be taken, since its value is close to unity if $V=0$ or if $V\neq 0$ but $c_\alpha\cong 1$, $c_\beta\ll 1$ (large positive values of V). Indeed, approximating the composition profile in the β phase by a linear function (see also Figs. 1 and 2): $\mathrm{grad}_\beta\, c\cong -c_\beta/X_\beta$,

$$J_\beta=z_v a\Gamma_0 c_\beta\exp(mc_\beta/2)/X_\beta. \tag{4}$$

Note that in the exponent, describing the composition dependence of D_β, the composition was taken to be $c_\beta/2$ since an average value (over the X_β distance) of D_β appears in Eq. (4).

Thus from the $J_\beta=J_I$ condition [see Eq. (3)], we can determine the thickness of the β phase where the transition of the kinetics from the linear changes to the parabolic one, i.e., the *changeover thickness* ($X^*\cong X^*_\beta$) is

$$\frac{X^*_\beta}{a}=\exp\left[\frac{mc_\beta}{2}+\frac{-\alpha_I+\varepsilon_I}{kT}\right]\frac{c_\beta}{\Delta c}. \tag{5}$$

In Eq. (5), c_β obviously means the composition in the β phase just at the interface, when the condition (5) fulfills. Although Eq. (5) is obtained for an exchange mechanism, a similar expression can be obtained for a vacancy mechanism (see Appendix A): $X^{*V}_\beta=\xi_1 X^*_\beta$ with ξ_1 having a value lying between 1 and 10 in practically important cases. This means that Eq. (5) gives a slight underestimation for X^*_β.

Note that, according to the mass conservation, there should exist a single relation between the shift of the interface ΔX and X_β: $\Delta X=c_\beta X_\beta/2$. However, since in the parabolic limit $J_I\gg J_\beta$, for the characteristic length of the interface shift, above which the parabolic limit is observed, one can take $\Delta X\cong 50c_\beta X_\beta/2$.

We have tested Eq. (5) by comparing the calculated X_β values to the results of our computer simulations and experimental results.[9–11,18,21,22] We found good agreement (see also Appendix B). For instance, if the diffusion coefficient is composition independent ($m=0$), the X^* changeover thickness is about $0.2a$, which coincides with simulations and analytical estimation given in Refs. 21 and 18.

When D is composition dependent and the system is completely miscible ($V=0$, $m\neq 0$, like Ni/Cu), we obtained that both the X^* and ΔX_c are several hundred atomic layers (about

300 nm) in reasonable agreement with the results of Refs. 9 and 11. If the system is not completely miscible ($V>0$, $m \neq 0$), Eq. (5) gives also realistic results. For example, in the Ni-Au system, X^* and ΔX_c are about $19a$ and $6a$, respectively, and both computer simulations[11] and experiments[22] indicate similar values.

We have found that the stronger the composition dependence of D (the larger the absolute value of m) at a fixed value of V, not only the value of X^* is larger but it has a more definite increase with decreasing temperature as well.

III. ATOMISTIC MEANING OF *K*

In order to derive an accurate form of the "interface transfer coefficient" K of *positive* sign (which would be necessary to obtain a linear growth law), a more detailed analysis of the steady state shape of the moving interface and the flux expression across such an interface would be necessary. Indeed, the steady state shape of the moving interface is determined not only by the value of V/kT. As was shown in Ref. 11 (see Fig. 4 there), if $|m|$ is large enough the interface could be even sharper than for a relatively strong phase separation tendency. This illustrates that the determination of K is a delicate problem.

However, following the phenomenological definition of K, $J_I=K(c_e-c)$ (c and c_e denote the current and the equilibrium composition at the interface, respectively), and comparing this to Eq. (2a), we can see that (taking $c_e=\langle c\rangle$ and $c \cong c_\beta$) K is just

$$K = z_v \Gamma_I \gamma_I (1+\varphi) \cong \nu z_v \exp(-Q_K/kT) \qquad (6)$$

with $Q_K=E_0+z_l V+MZ=E_0+z_l V+mkT/2$.

In fact, the above approximation, together with the assumption on the diffusion current $J_D=D\Delta c/X^*\Omega$ with $\Delta c=1$ and $c_e-c\cong 1$, was used in Ref. 1 to get an order of magnitude estimate of X^* from the $J_I=J_D$ condition as $X^*=D/K\Omega$. In this case, the composition dependence of the jump frequencies was neglected ($m=0$), i.e., $D_\alpha=D_\beta=z_v\nu a^2\exp(-E_0/kT)=D_0\exp(-Q_D/kT)$ was assumed.

It can be seen from Eq. (2a) that K is proportional to the jump frequency from the A-rich phase to the B-rich one. This is different from the jump frequency in the B-rich phase (where the jump frequencies are larger at the same temperature) just because these frequencies depend on the composition. If there is an abrupt interface present at the very beginning of the intermixing, then the interface transfer controls the flux only until the gradients will be large enough to establish the diffusion flux J_β larger than J_I. In fact, the magnitude of the finite value of $J_I \cong K$ gives the permeability of the interface and it is determined by the m and V/kT parameters.

It is important to emphasize that this interpretation is forced by the demand that one would like to express the fluxes by the classical $J \propto -\text{grad}\,\rho$ form. In fact, the validity of Fick's I equation gradually breaks down with decreasing diffusion distances, and in the "improved" forms of the continuum expressions of the atomic fluxes, higher order derivatives of the composition should appear.[10,16] These should lead to a "slowing down" of the flux and this can be taken into account by such a treatment presented above. Thus the $1/\sqrt{t}$ dependence of the rate of the shift will be violated on the nanoscale just because the classical continuum description fails and for strongly composition dependent jump frequencies (for large $|m|$ values) even a linear shift can be experimentally observed.

There are important differences between the approaches used in Ref. 8 (which is, to our knowledge, the only work trying to give an atomistic explanation of K) and presented here. In our approach, the nanoscale effects and the effects of the strong composition dependence of the diffusion coefficients (strong diffusion asymmetry) were specially addressed. We derived an expression for the interface transfer coefficient of *positive* sign and show that this is proportional to the atomic jump frequency across the interface. In fact, K is the measure of the finite permeability of the interface and thus it controls the growth rate of the diffusion zone at short times. In Ref. 8, a *negative* K was derived from the introduction of a sharp Gibbsian interface instead of the real (wider) one.

The above considerations were made for coherent interfaces. In most of the real cases, noncoherent interfaces are present in the diffusion zone and then other factors (e.g., activity of vacancy sources and sinks in the interface[23–25] in case of vacancy mechanism of diffusion) can also play an important role to make the transfer of atoms across the interface sluggish enough[6,26] to control the process. These effects, however, are rare or must be in the same order of magnitude as the effects considered above, since on the *micrometer* scale clear experimental evidence for deviations from the parabolic behaviors is very rare.[2] On the other hand, our results illustrate that the shift of the interface can be different from the parabolic behavior just because the permeability of the interface is finite, and this can already lead to measurable effects in the interface kinetics on the nanoscale. Thus effects of other factors, if at all (like problems with sluggish structural rearrangements in noncoherent interfaces), in making the atomic transfer more restrained should be additionally considered. However, then an extra activation barrier should be included into the atomistic model description, which was not the case here.

IV. CONCLUSIONS

In our paper, we offer a natural resolution for a long-standing paradox in diffusion. We have shown that the growth rate of the diffusion zone (reaction layer) should not go to infinity with decreasing time (as $1/\sqrt{t}$), just because the diffusion permeability of the interface (being sharp either because of the presence of a miscibility gap, or because of the large diffusion asymmetry, or because there is an abrupt jump of the composition in the diffusion couple at the beginning) is finite. An expression for the changeover thickness X^* between the linear and parabolic regimes of the interface shift in ideal or phase separating binary $A(B)$ systems has been derived. It was found that X^*, depending on the phase separation tendency and the diffusion asymmetry (measured by the strength of the composition dependence of the diffusion coefficients), lies between 0.01 and 300 nm, illustrating that these effects can be measurable on the nanoscale.

The atomistic meaning of the interface transfer coefficient K across coherent interfaces has also been discussed. It has been shown that it is positive and proportional to the jump frequency from the A-rich phase to the B-rich one, i.e., it is a measure of the finite permeability of the interface.

Although it is almost exclusively accepted in the literature that linear growth kinetics are the result of interface reaction control, our results suggest that the linear or nonparabolic growth of a reaction layer on the nanoscale cannot be automatically interpreted by an interface reaction. Indeed linear kinetics has been observed even in ideal systems (e.g., Ni/Cu, see Ref. 9), where a classical interface (separating two phases) does not exist or deviation from the parabolic law has been obtained in Ni/Au system[22] where a well-defined chemical interface is present according to the miscibility gap. Plausibly, the above conclusion, in contrast to the well-known arguments in handbooks on diffusion, where linear or almost linear kinetics are interpreted by interface reaction control, should also be applied for phase growth kinetics in many solid state reactions.

ACKNOWLEDGMENTS

This work was supported by OTKA Grants No. T-038125, K61253, and F-043372. Z. Erdélyi acknowledges support from Bolyai János Foundation.

APPENDIX A: BASIC EQUATIONS FOR VACANCY MECHANISM

According to Ref. 27, in case of a vacancy mechanism, the change in composition of A or B in plane i is given by

$$\frac{dc_i^K}{dt} = J^K_{i-1,1} - J^K_{i,i+1}, \quad K = A,B,$$

where $J^K_{i,i+1}$ is the net flux of K atoms from layer i to $i+1$ and is defined as

$$J^K_{i,i+1} = z_v[c_i^K c_{i+1}^V \Gamma^K_{i,i+1} - c^K_{i+1} c_i^V \Gamma^K_{i+1,i}].$$

Here, e.g., c_i^K and c_i^V are the fractions of K atoms and vacancies, respectively, in the ith layer (obviously $c_i^A + c_i^B + c_i^V = 1$). The atom-vacancy exchange frequencies can be given by expressions such as

$$\Gamma^K_{i,i+1} = \nu \exp\left(-\frac{E^K_{i,i+1}}{kT}\right), \quad K = A,B.$$

In principle, $E^K_{i,i+1}$ is the activation barrier for the atom-vacancy exchange, which is equal to $-E_i^K$, i.e., the negative value of the energy of the K atom in the layer i, and can be given by

$$E_i^K = z_v[(c^A_{i+1} + c^A_{i-1})V_{AK} + (c^B_{i+1} + c^B_{i-1})V_{KB}] + zl(c_i^A V_{AK} + c_i^B V_{KB}).$$

Here we note that the A atom-vacancy ($\Gamma^A_{i,i+1}$) exchange usually differs from the B atom-vacancy ($\Gamma^B_{i,i+1}$) exchange frequency, i.e., the intrinsic diffusion coefficients are different in this model, which are each composition dependent. If they are not equal to each other, Kirkendall shift should also appear in real systems. However, for lack of vacancy sinks and sources, its treatment is not possible in this atomistic model at present.

After some algebra it can be shown that, e.g.,

$$\Gamma^A_{i,i+1}\omega_{i+1} \cong \Gamma_{i,i+1} \quad \text{and} \quad \Gamma^A_{i+1,i}\omega_i \cong \Gamma_{i+1,i},$$

where

$$\omega_{i+1} = \exp\left(-\frac{E^B_{i+1}}{kT}\right) \quad \text{and} \quad \omega_i = \exp\left(-\frac{E^B_i}{kT}\right). \tag{A1}$$

The approximate equality in Eqs. (A1) means that we neglect c_i^V's compared to c_i^K's in additive compositions since $c_i^V \ll c_i^K$. Using these equations, the net flux across the interface can be written as

$$J_I^A = z_v \Gamma_I \gamma_I \left[\langle c^A \rangle c_\beta^V \frac{1}{\omega_1} - c_\beta^A \langle c^V \rangle \frac{1}{\omega_2 \gamma_I^2}\right].$$

Here ω_1 and ω_2 are obtained from ω_{i+1} and ω_i, respectively, applying the same assumptions as in Sec. II B. Using that the vacancy composition of layer i can be calculated as[27]

$$c_i^V = (1 - c_i^A)\exp\left(Z\frac{V_{BB} + c_i^A(M+V)}{kT}\right),$$

we arrive at the following expression of J_I^A

$$J_I^A = z_v \Gamma_I \gamma_I \xi_1 (1 + \varphi^V)\Delta c^A$$

with

$$\varphi^V = \frac{c_\beta^A(1 - \langle c^A \rangle)}{\Delta c^A}\left(1 - \frac{\xi_2}{\xi_1}\right)$$

and

$$\xi_1 = \exp\left\{-[z_v\langle c^A \rangle + (z_l - 1)c_\beta^A]\frac{M+V}{kT}\right\},$$

$$\xi_2 = \exp\left\{-[z_v(c_\beta^A + 1) + (z_l - 1)\langle c^A \rangle]\frac{M+V}{kT}\right\}.$$

Neglecting φ^V compared to 1 leads here also to an error of maximum 25%. Thus using again the same condition to determine the transition thickness ($J_I^A = J_\beta^A$), we obtain that

$$X_\beta^{*V} = \xi_1 X_\beta^*. \tag{A2}$$

This means that the transition thickness deduced from direct exchange or vacancy assisted mechanism diffusional considerations differs only by the ξ_1 factor, which has a value of ~1–10 in practically important cases [for example, $\xi_1 \cong 11$ for a Ni/Cu-like system (see Appendix B, case (b)) and $\xi_1 \cong 2$ for a Ni/Au-like system (see Appendix B, case (d))]. Thus the conclusions obtained for exchange mechanism are qualitatively valid for a vacancy mechanism as well, and the crossover thickness is even larger in the latter case by the factor of ξ_1.

Finally, note that Eq. (6) is also modified accordingly

$$K^V = z_v \Gamma_I \gamma_I \xi_1 (1 + \varphi^V) \cong \nu z_v \exp(-Q_K/kT)$$

with $Q_K = E_0 + (z_l - z_v)V + (z_l + z_v)M = E_0 + (z_l - z_v)V + (z_l + z_v)/(2Z)mkT$.

APPENDIX B: NUMERICAL ESTIMATIONS OF THE CHANGEOVER THICKNESS

In this section, the changeover thicknesses are determined using Eq. (5), which is obtained for a direct exchange mechanism. However, as can be seen from Eq. (A2), the changeover thicknesses are in the same order of magnitude for vacancy mechanism, too.

(a) $m=0$ and $V \neq 0$. For large values of V/kT it is expected that c_β will correspond to the solubility limit and taking a symmetrical miscibility gap $(1-c_\alpha=c_\beta)$, c_β can be estimated from the well-known expression, obtained from a continuum regular solid solution model: $c_\beta = (1-c_\beta)\exp[-ZV(1-2c_\beta)/kT] \cong \exp[-ZV/kT]$. Furthermore, in this case, $\langle c \rangle \cong 1/2$ can be put into Eq. (5) and due to the symmetry of the diffusion profile, $X^*_\alpha = X^*_\beta \gg X^*_I$. Thus, taking $z_l = z_v = 4$, e.g., for $V/kT=0.36$ as well as $V/kT=0.5$, $X^*=0.12a$ and $X^*=0.04a$, respectively. Although the obtained numbers for X^* are very low to be experimentally measurable, the result that the changeover thickness decreases with increasing V is in accordance with the results of simulations obtained in Ref. 11. In the beginning of the dissolution of the slower component into the matrix of the fast diffuser, the deviation from the parabolic law was stronger for smaller V values.

(b) $V=0$ and $m \neq 0$. Now we can assume that for large absolute values of m, c_β is still $\ll 1$ (in the order of $10^{-1}-10^{-2}$, see Fig. 1 of this paper and also Fig. 26 in Ref. 10 for Ni/Cu system with $m=-22.3$), i.e., we can take $c_\beta = 0.05$. [In ideal systems, the value of c_β in Eq. (5) means the value belonging to the kink of the composition profile when the condition $J_\beta = J_I$ just fulfills.] It was found also in Ref. 9 that $\langle c \rangle = 0.78$ (for $z_l=6$, $z_v=3$). Thus, we get $X^* \cong X^*_\beta = 658a$, which is in good accordance with the results of simulations of Refs. 9 and 10: the transition from the linear to parabolic shift took place after dissolution of several hundred atomic planes. Indeed, $\Delta X_c = 823a$, which agrees well with this result. In order to illustrate the effect of the choice of c_β, here are the results for $c_\beta=0.025$ and $c_\beta=0.1$: $X^*=341a$ and $X^*=1230a$, respectively.

(c) $m=0$, $V=0$. The composition profile will be symmetrical and thus $\langle c \rangle = 1/2$. The changeover thickness is $X^* = 2X^*_\beta = 2ac_\beta/\Delta c$. Since it is expected that c_β will be in the order of 0.05, $X^* \cong 0.2a$. This can be compared with $X^{*\prime} \cong 6a$, obtained from the condition that the difference between the composition profiles, calculated from the classical Fick II law and from the atomistic equations of diffusion in multilayers, should be less than 2%.[18,21] Since X^*_β denotes the thickness of the diffusion zone in the β phase, at which the above two currents (J_I at the beginning and J_β in the long time limit) are equal to each other, while the $X^{*\prime}=6a$ condition belongs to the limit when the process can be dominantly described by Eq. (4), they agree reasonably well.

(d) Intermediate cases. For general cases (when both V and m are different from zero), a more detailed analysis of the shape of the moving interface would be necessary to estimate the c_β and $\langle c \rangle$ compositions. Fortunately, following the calculation procedure described in Ref. 9, one can do the estimation of $\langle c \rangle$. Furthermore, for large V/kT values, c_β can be calculated from the regular solid solution model, and numerical simulations of c_β are necessary only for small V/kT and large m values. For example, taking the $V/kT=0.36$ and $m=-13.8$ values, used also in the simulations of Ref. 11 for $z_l=z_v=4$, it was obtained that $\langle c \rangle = 0.685$ and $c_\beta=0.013$. Thus $X^* \cong X^*_\beta = 19a$. Now, it was found from experiments[22] that in Au/Ni system (for which the input parameters above suit very well), the time dependence of the shift of the interface indeed followed the $t^{0.63}$ law, i.e., it was between a linear and parabolic behavior during the dissolution of about six atomic planes. This is in a good agreement with $\Delta X_c = 6a$. In order to illustrate that the certain arbitrariness in the choice of c_β still does not have a big influence on the estimated value of X^*, we give two results for $m=-13.8$, $V/kT=0.09$ (almost ideal system) with $z_l=z_v=4$: $X^*=23a$ and $87a$, for $c_\beta=0.05$ and 0.2, respectively.

(e) Temperature dependence of X^*. It can be seen that in case (a) X^* decreases with decreasing T. On the other hand, it follows from Eq. (5) that in case (b) ($V=0$, and $m=-22.3$ and thus taking as above $c_\beta=0.05$ and $\langle c \rangle = 0.78$), X^* increases with decreasing temperature, while for case (c) (both V and m are zero) X^* is independent of T. Finally, in case (d) if $V/kT=0.36$ and $m=-13.8$, there is a weak temperature dependence because the two factors [corresponding to the temperature dependence of the solubility limit as well as to the factor containing m in the exponent of Eq. (5)] will compensate each other, although still there is a small increase in X^* with decreasing temperature.

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