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Stress effects on diffusional interface sharpening in ideal binary alloys

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As an extension of our previous paper [Phys. Rev. Lett. **89**, 168901 (2002)], we demonstrate, using computer simulations based on a general continuum model, that the diffusional interface sharpening in ideal binary alloys (found recently from deterministic kinetic equations in discrete atomic approach) is still present even if the stress development and relaxations during interdiffusion or if the "built-in" stresses (caused by lattice mismatch or thermal expansion) are also taken into account. Thus we conclude that this diffusional sharpening, in systems with large diffusion asymmetry, is really a quite general phenomenon.

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Very recently, using computer simulations based on deterministic kinetic equations[1] and Monte Carlo technique, we demonstrated[2] that on nanoscale (short diffusion distances, short time) and for strongly concentration dependent D (large diffusion asymmetry), an initially wide A/B interface can become sharp even in an ideal system. It was also shown in our previous paper[2] that in principle the continuum flux equations are also capable of describing the sharpening, at least qualitatively.

However, in calculations mentioned above, stress effects were not included, although they can be very important in thin films or multilayers. Thus it is an interesting question, how these effects can influence the diffusional interface sharpening.

The problem addressed is interesting not only form the point of view of fundamental research. For example, the Ni/Cu system is a model material for giant magnetoresistence (GMR), multilayers made from Mo and V (which is also an ideal binary system) are model materials for x-ray mirrors, and in these systems the abruptness of the interface, and the knowledge of the possibilities for its improvement, is a key point. It is also well known that in MBE (molecular beam epitaxy) grown Si-Ge multilayers the Ge/Si interface, produced by the deposition of Si on Ge, is always less sharp (due to the mixing driven by the segregation of Ge during the growth) than the Si/Ge interface.[3,4] The sharpening effect described here offers a way for the improvement of the multilayers and the diminution of the asymmetry by annealing at moderate temperatures for relatively short times.

Since the treatment of stress effects is not well developed for the discrete, atomistic kinetic approach,[5–7] one can investigate the problem in the framework of continuum models only. Although the continuum model describes the sharpening qualitatively (and, e.g., it cannot give account of the initial linear shift of an originally sharp interface on nanoscale[8,9] and the time scale obtained from this can differ from the real one[10]), from calculations based on these models one can get an inside view of stress effects on interface sharpening.

Basically three types of stresses can be considered: (i) *built-in stress* originating from the lattice mismatch at the interface, (ii) *thermal stress* due to the difference between the thermal expansion coefficients of the layers,[11] and (iii) *diffusional stress* developing during interdiffusion because of the net volume transport caused by the difference of atomic currents of the constituents through the interface. Thus, we have performed computer simulations using Stephenson's[12] model in which the above types of stresses can be treated and stress relaxation is also considered.[13] Stephenson—in a one-dimensional, isotropic binary system—derived a set of coupled differential equations for the description of the resultant stress development and stress relaxation by viscous flow, convective transport (Kirkendall shift), and composition evaluation:

$$\frac{DP}{Dt} = -\frac{2E}{9(1-\nu)}\left[\sum_{1=1}^{2}(\Omega_i \nabla j_i) + \frac{3}{4\eta}P\right], \tag{1}$$

$$\nabla v = -\sum_{1=1}^{2}(\Omega_i \nabla j_i) - \frac{3(1-2\nu)}{E}\frac{DP}{Dt}, \tag{2}$$

$$\frac{Dc}{Dt} = -\frac{1}{\rho}[(1-c)\nabla j_1 - c\nabla j_2], \tag{3}$$

where P is the pressure, t the time, E Young's modulus, Ω_i the atomic volume of the constituents $i(=1,2)$, η the share viscosity, v the Kirkendall velocity, c the atomic fraction of material 1, ρ the average volume density, and j_i the atomic flux, which is given by[14,13]

$$j_i = -\rho D_i \nabla c - \rho^2 D_i \frac{\Omega_1 \Omega_2}{RT\Theta} c \nabla P, \quad i=1,2. \tag{4}$$

Here D_i is the intrinsic diffusion coefficient, R the molar gas constant, T the absolute temperature, and Θ the thermodynamic factor. Note that in this paper we restrict ourselves to an ideal binary system, i.e., $\Theta = 1$. Otherwise the gradient energy effect should also be taken into consideration and an additive term should be included in Eq. (4).[13] In general, two types of pressure effects on diffusion can be taken into account. One of them is the pressure dependence of the diffusion coefficient [$\propto \exp(-PV/kT)$,[15] where V is the activation volume and k is Boltzmann's constant] and the second one is the effect of stress (pressure) gradient on the diffusion flux, which is manifested in Eq. (4). Note that in our calculations only the last effects is considered.

We performed simulations for three different cases. First, only the stress due to the net volume transport was consid-

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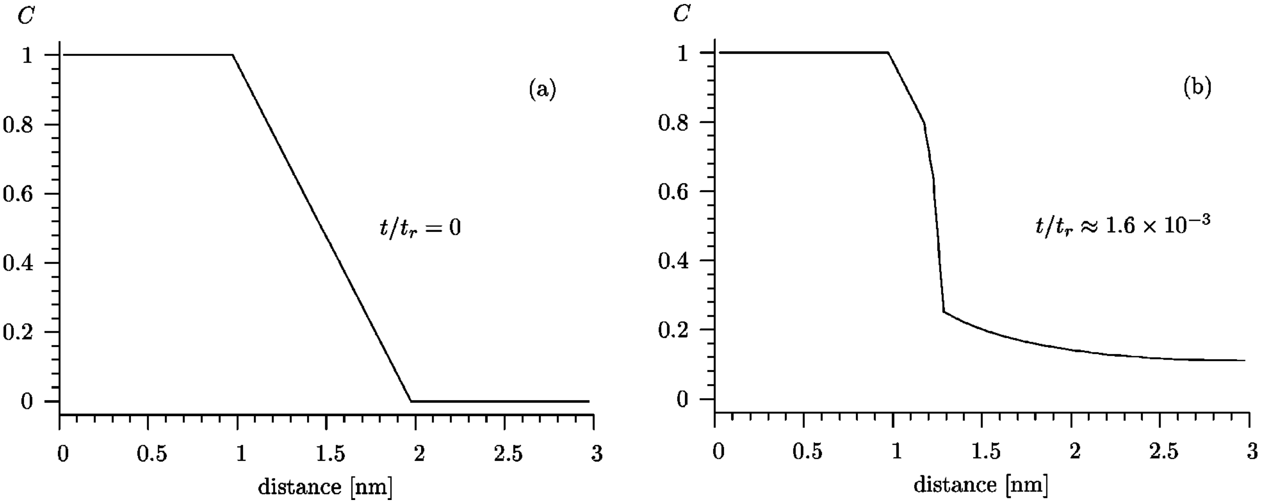

FIG. 1. Time evolution of the composition profile of Mo, at two different normalized times, when all the stress effects are ignored.

ered. Second, the thermal stress was also taken into account and finally the built-in stress was additionally considered as well. In all the cases the input parameters were chosen close to that of a Mo-V multilayer system (Young's modulus, $E_{\mathrm{Mo}}=324.8$ GPa, $E_{\mathrm{V}}=127.6$ GPa; Poisson's ratio, $\nu_{\mathrm{Mo}}=0.293$, $\nu_{\mathrm{V}}=0.365$; viscosity, $\eta_{\mathrm{Mo}}\approx\eta_{\mathrm{V}}=1.689\times10^{15}$ Pa s; molar atomic volumes, $\tilde{\Omega}_{\mathrm{Mo}}=9.4\times10^{-6}$ m^3/mol, $\tilde{\Omega}_{\mathrm{V}}=8.36\times10^{-6}$ m^3/mol; coefficients of thermal expansion, $\alpha_{\mathrm{Mo}}=2.7\times10^{-6}$ K^{-1}, $\alpha_{\mathrm{V}}=8.5\times10^{-6}$ K^{-1}; $T=1053$ K).[10,13,16] Note that in this work the parameters E and η are considered composition independent for the sake of simplicity although in reality they depend on it. We, however, think that this simplification does not influence our later qualitative consequences. Moreover, the value of viscosity does not play a role important as it determines only the stress relaxation time (see later), which is higher by many orders of magnitude than the time scale investigated.

According to our previous calculations,[2] we supposed exponential composition-dependent diffusion coefficients: $D_{\mathrm{Mo}}=D^0_{\mathrm{Mo}}\exp(-mc)$; $D_{\mathrm{V}}=2D_{\mathrm{Mo}}$. The modulation length of the multilayer was 6 nm, the initial width of the interface between the Mo and V layers was 1 nm.

Figure 1 shows the time evolution of the composition profile when all the stress effects are ignored, and beside the "filling up" of V by Mo, there is indeed interface sharpening, similarly as observed in Ref. 2. The time scale is normalized; t_r is the stress relaxation time (see below).

In Fig. 2, the sample is stress-free initially and during the mixing a stress peek develops on the Mo side close to the interface and on the V side an almost homogeneous stress field (with opposite sign) appears. This is because the Mo atoms near the interface can easily dissolve into the V and diffuse there, whereas the V atoms practically cannot penetrate into the Mo (diffusion asymmetry due to the strong composition dependence of D's). Note that in this case for the sake of simplicity in Eqs. (2) and (3) the average values of E's and ν's were used.

Figure 3 shows the results of calculations for the case when, in addition to the stress development shown on Fig. 2, the initial stress profile is a result of the different coefficients of thermal expansion of the constituents. To estimate it, we used a continuum model[17] according to which the stress can be given along the z axis by

$$\sigma(z)=\frac{E(z)}{1-\nu(z)}[\varepsilon_0-\alpha(z)\Delta T], \tag{5}$$

where $E(z)=V_{\mathrm{Mo}}(z)E_{\mathrm{Mo}}+V_{\mathrm{V}}(z)E_V$ and $\alpha(z)=V_{\mathrm{Mo}}(z)\alpha_{\mathrm{Mo}}+V_{\mathrm{V}}(z)\alpha_{\mathrm{V}}$. Here V_{Mo} and V_{V} are the volume fraction of Mo and V, respectively. In Eq. (5) ε_0 denotes the strain at $z=0$, and it can be calculated from the equilibrium condition $\int_0^h\sigma(z)\mathrm{d}z=0$, where h is the thickness of the sample. Note that in a multilayer system, in which the composition varies only one in dimension (z direction), $\sigma_{zz}=0, \sigma_{xx}=\sigma_{yy}=\sigma\neq0$, and thus $\sigma=-\frac{3}{2}P$ (see, e.g., Ref. 12). Moreover, since Mo-V epitaxial multilayers are usually prepared at about 953 K,[18,19] here $\Delta T=100$ K. It can be seen that the composition profiles shown in Fig. 2 and 3 are very similar. (Calculations for $\Delta T=500$ K gave practically the same result.) We have

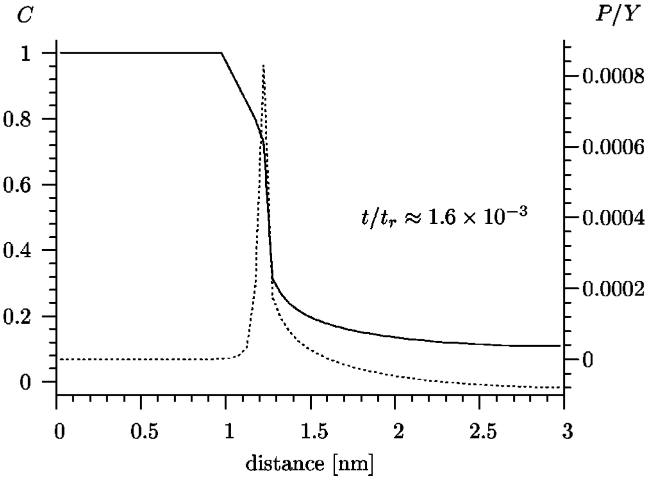

FIG. 2. Time evolution of the composition profile of Mo at $t/t_r=1.6\times10^{-3}$ when only the diffusional stress ($D_V/D_{Mo}=2$) is taken into account [The initial state is the same as in Fig. 1(a)]. The dotted line is the normalized pressure [P/Y where $Y=E/(1-\nu)$].

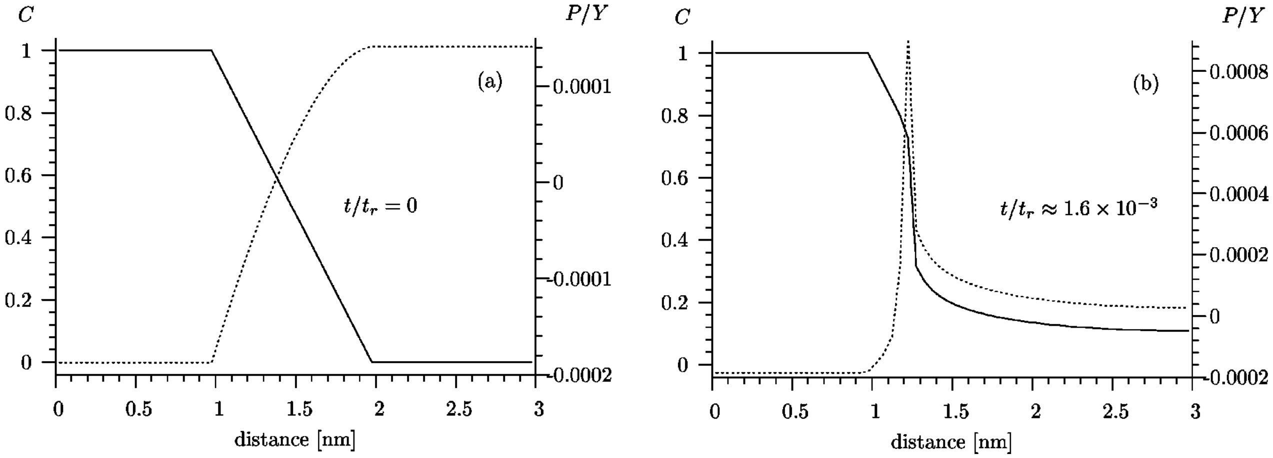

FIG. 3. Time evolution of the composition profile of Mo considering the thermal stress ($\Delta T = 100$ K) as well (see for comparison Fig. 2). The dotted line is the normalized pressure $[P/Y$ where $Y = E/(1-\nu)]$.

repeated the above calculation taking into account the built-in stress as well, including a strain term proportional to the difference of the lattice parameters; however, any difference from the previous cases was not observable.

Finally note that the $t/t_r > 0$ curves in all the figures correspond to the same reduced time ($t/t_r = 1.6 \times 10^{-3}$). It can be seen that the stresses did not modify significantly the time scale of the process, either. It is, however, not a trivial result because usually the stress effects slow down the intermixing.[13,20]

The time evolution of the effect of diffusional stresses, playing dominating role above, can be classified into four different stages in symmetric systems (with $m = 0$): (i) $t < t_{Qss}$, (ii) $t_{Qss} < t < t_r$, (iii) $t \approx t_r$, and (iv) $t \gg t_r$. Here t_r is the stress relaxation time of "pure" Newtonian flow[12,14] (determined by η): $t_r = 6\eta(1-\nu)/E = 2.59 \times 10^4$ s [see also the second term in Eq. (2)]. On the other hand t_{Qss} is the time necessary to develop a steady state stress distribution. In stage (ii)—at least in systems with $m = 0$—the stress distribution is almost symmetrical[20] [see also Fig. 4(b)], and, if the resultant volume flow (measured by $\Omega_V D_V / \Omega_{Mo} D_{Mo}$) is large, the slowing down of the intermixing is expected because the stationary stress gradient tends to diminish the volume flow itself.[20] Furthermore, in stage (i) the stress gradient in the central zone [where the composition falls: see Fig. 4(a)] plays the dominating role and effectively decreases the net volume transport already for $t < t_{Qss}$.

In order to illustrate the situation for our asymmetric case, Fig. 5 shows the results for $D_V/D_{Mo} = 2$ and $D_V/D_{Mo} = 10$ (for five times larger volume flow as before). It can be seen that in the second case the slowing down effect is already visible, but the sharpening is still present (obviously with a slower rate). It is important to note that the condition $t \ll t_r$ is always fulfilled, but in Figs. 2 and 3(b) still $t < t_{Qss}$, and the pressure peak at the interface slowly increases and reaches its maximum value only when the interface becomes sharp ($t_{Qss}/t_r \approx 9.5 \times 10^{-3}$). Thus we are in the stage (i) during the interface sharpening, and then, when the sharp interface shifts, in (ii). [Stages (iii) and (iv) cannot practically be reached because during the time $t/t_r \approx 0.2$ two-thirds of the Mo layer has already been consumed.] In stages (i) and (ii) the first term in Eq. (2) determines the stress relaxation (and thus our calculations were not sensitive to the choice of η) and this is why the stress distribution is very asymmetric: the

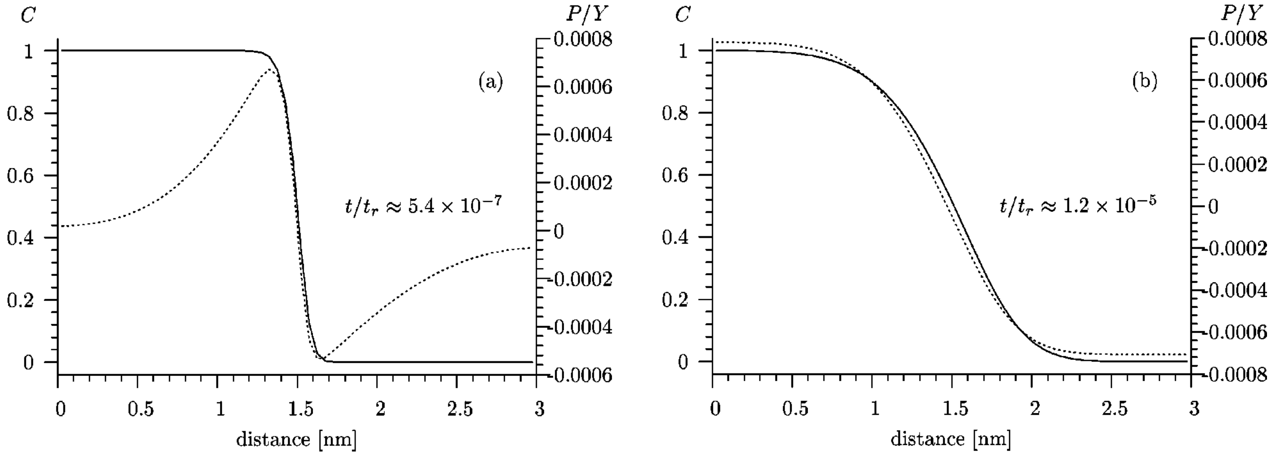

FIG. 4. Time evolution of the composition profile of Mo considering only the diffusional stress for $m = 0$ and $D_V/D_{Mo} = 2$. The dotted line is the normalized pressure $[P/Y$ where $Y = E/(1-\nu)]$. (a) $t < t_{Qss}$ ($t_{Qss}/t_r \approx 9.5 \times 10^{-3}$), (b) $t_{Qss} < t < t_r$.

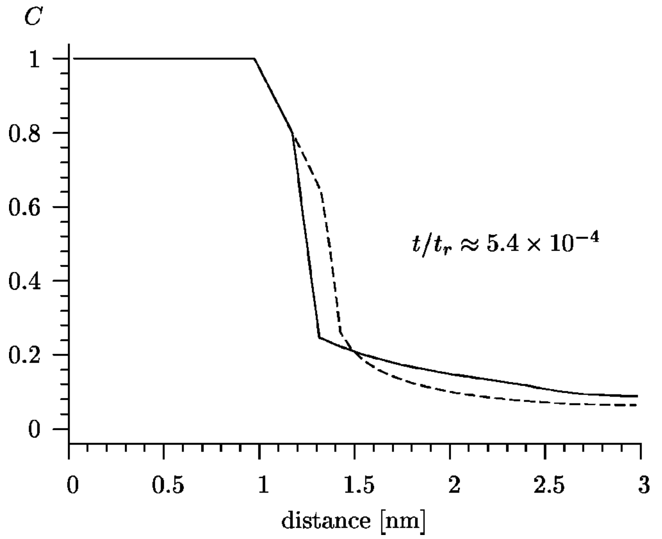

FIG. 5. Demonstration of the influence of the strength of the diffusional stress: $D_V/D_{Mo}=2$ solid line, $D_V/D_{Mo}=10$ dashed line.

stress relaxation is fast in the V and practically there is no relaxation in the Mo. Thus, here—instead of the slowing down by a stress gradient formed in symmetric systems—the effect is due to the presence of the pressure peak in the Mo side just at the sharp interface formed (see, e.g., Fig. 2). The pressure peak shifts with the moving interface. In stage (ii) the height of the pressure peak is almost constant (it decreases only because of the finite size of the V layer). However, the resultant volume flow is practically compensated here as well (the very small changes in the height of the pressure peak indicates it): in this sense the symmetric and asymmetric case do not differ and in both the LeChatelier-Braun principle is fulfilled: the diffusion induced stresses compensate the effect generating them.

In conclusion, comparing the results of calculations shown in Figs. 2–5 one can conclude that in all cases (independently whether stress effects were included or what kind of their initial distribution were assumed) the interface sharpening took place. Furthermore, it was illustrated that the intermixing took place approximately in a steady state regime in which the slowing down effect, known in symmetric diffusion systems, can be also present (but with an asymmetric stress distribution) if the resultant volume flow is large enough. Even in this case the sharpening was also observed (obviously with a slower rate).

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