

Nonequilibrium Roughening of Interfaces in Crystals under Shear: Application to Ball Milling

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(Received 18 July 1994)

A simple kinetic atomistic model is proposed for describing crystals submitted to sustained shearing, acting in competition with thermally activated diffusion. Monte Carlo simulations are performed on alloys with positive heats of mixing. The results provide a clear understanding of recent experiments showing that chemical mixing of immiscible elements can be induced by ball milling. At moderate shearing rates, an analytical model shows that such driven systems exhibit nonequilibrium roughening.

PACS numbers: 81.40.-z, 05.40.+j, 68.35.Fx

The behavior of surfaces and interfaces in open dissipative systems has recently received much attention (for a review see [1]) owing to its relevance for kinetic roughening during such processes as thin-film deposition, oxidation, and sputtering. In these situations an external forcing introduces a microscopic perturbation at a surface or interface which acts in competition with some relaxation process. We consider here the related case where the perturbation introduced by the external forcing has a macroscopic component, such as for crystals submitted to sustained shearing. This type of forcing has also become of interest, as mechanical alloying has been shown to be an important method for synthesizing nonequilibrium phases (for a review see [2]). It was noted previously that phase transformations taking place in such driven systems must be analyzed from the point of view of a nonequilibrium dynamical system [3–5].

To illustrate how shearing leads to phase formation and to elucidate the role of kinetic roughening at interfaces in this process, we propose a simple atomistic kinetic model. Consider a crystal where atoms are allowed to move because of two mechanisms acting in parallel: Atoms are shifted by shears along randomly selected glide planes, while, concurrently, individual atoms exchange sites with vacancies via thermally activated jumps. As an example of the model, Monte Carlo simulations were performed on a rigid lattice for alloys having large miscibility gaps. This example is particularly germane since it is presently controversial how solid solutions can be formed in these systems by ball milling, e.g., Cu-Fe [6] or Cu-Co [7]. We will show that, during shearing, planar interfaces become increasingly rough, leading to refinement of the microstructure and eventually to complete chemical mixing of the system. We will then use the procedure introduced by Edwards and Wilkinson [8] to construct an analytical model for studying interfacial roughening in crystals under shearing. We will show that, owing to the macroscopic component of the perturbation introduced by shearing, the usual dynamical scaling obtained in models describing surface growth [9,10] is not obeyed.

A simple measure of the intensity γ of the external forcing in our model system is the ratio of the forced jump frequency to the thermally activated one. Two

limiting cases are rather trivial: (i) for $\gamma = 0$, thermally activated diffusion will drive the system to its equilibrium state, and (ii) for infinitely large γ , the system transforms to a random solid solution. We therefore focus on the behavior at intermediate values of γ .

For the Monte Carlo simulations, a face centered cubic (fcc) crystal was constructed from an $N \times N \times N$ ($N = 16$ to 64) simple rhombohedral crystal with periodic boundary conditions. The faces of the rhombohedron correspond to $\{111\}$ planes of the fcc crystal. An $A_{0.5}B_{0.5}$ alloy is considered. A and B atoms interact with their nearest neighbors through pair potentials ϵ_{ij} (i and j equal A and B). The potentials are chosen to reproduce an estimated critical temperature of 1573 K in the Cu-Co system; we thus set $V = \epsilon_{ii} + \epsilon_{jj} - 2\epsilon_{ij} = -0.05533$ eV [11]. The equilibrium phase diagram resulting from this choice of potentials has been previously published [12]. A single vacancy is then introduced into the crystal. The rate of exchange between this vacancy and nearest-neighbor atoms is computed using standard rate theory [13]. The activation energy for vacancy motion is the energy required to break the bonds between the jumping atom and its surroundings less the energy recovered when the atom is placed at the saddle point position. These frequencies obey detailed balance. For simplicity, we set $\epsilon_{AA} = \epsilon_{BB}$. The only relevant parameters are then ν (set to 10^{15} s $^{-1}$ for reproducing a typical preexponential diffusion coefficient of $D_0 = 10^{-4}$ m 2 s $^{-1}$) and the saddle point energy E_s (chosen to give a vacancy migration energy of 0.8 eV in pure A or pure B).

A residence-time algorithm is used to select the next atom to be exchanged with the vacancy [14]: this makes it possible to follow the evolution of the system in physical time, measured in seconds. The time between two shearing events is chosen at random so as to reproduce a selected average shearing frequency. Because of the periodic boundary conditions, shears are introduced in pairs, i.e., a slice of the crystal is shifted with respect to the remaining crystal. For each shearing event the following parameters are selected at random: one of the four $\{111\}$ planes of the fcc crystal for determining the active glide system, one of the six nearest-neighbor vectors lying in this plane for determining the vector of

the shift to be applied, and the locations of the first and last planes to be shifted. A quantitative comparison with experiments is difficult since the actual shearing rates during ball milling can only be roughly estimated, and since the nonequilibrium vacancy concentration reached under plastic deformation depends on time, temperature, shearing rate, and microstructure [15,16]. As we are here interested in the qualitative evolution of the steady states on going from near equilibrium to far from equilibrium situations, we keep constant the vacancy concentration in the simulations. For quantitative comparisons, rescalings of time and shearing rate will be necessary. From the analytical model discussed below, it is shown that a rescaling of the shearing rate will not affect the sequence of steady states.

For characterization of interfaces, the following procedure was used: A coarse graining of the initial rhombohedron lattice of parameter a into a simple cubic lattice of parameter $\sqrt{2}a$ was performed; a site in this coarse-grained lattice belonged to the B -rich phase whenever its local concentration of B atoms was larger than 0.5 (as measured by counting up to second nearest neighbors of the fcc lattice); the B -rich phase was easily identified as the largest connected set of such sites; interfacial sites on this coarse-grained lattice were those which had at least one neighbor belonging to the opposite phase. When interfaces do not contain any overhang, the height of the interface at position $\mathbf{r} = (x, y)$ is given by a single-value function Z_r , and we calculate height-to-height correlation functions $G(|\mathbf{r}|, t) = \langle [Z_{\mathbf{r}_0}(t) - Z_{\mathbf{r}_0 + \mathbf{r}}(t)]^2 \rangle^{1/2}$ (the brackets denote an average over all possible \mathbf{r}_0 and a spherical average over \mathbf{r}) and their Fourier transform.

Figure 1 illustrates typical steady-state configurations obtained at a temperature $T = 400$ K on increasing the shearing rate γ_{sh} : while a flat (111) interface between almost pure A and pure B bulk phases is stable at very low γ_{sh} values, (a) for $\gamma_{sh} = 1 \text{ s}^{-1}$ the interface remains sharp at the atomic scale, but now it exhibits undulations; (b) for $\gamma_{sh} = 10^{+3} \text{ s}^{-1}$ a refined microstructure is observed; however, the two phases are still distinguishable and fully connected; (c) for $\gamma_{sh} = 10^{+5} \text{ s}^{-1}$ a nearly random solid solution is stabilized, as indicated by the small value of the first Warren-Cowley short range order parameter [12] $\alpha_1 = 0.1145$. From this sequence and the kinetic paths taken by the system, it is seen that there are two different types of mixing in the alloy. At moderate shearing rates [Figs. 1(a) and 1(b)], the interface remains sharp but the initial flat interface is unstable and develops undulations. Atomic mixing remains incomplete; in fact, the mutual solubilities increase only to $\approx 0.1\%$. At high shearing rates [e.g., in Fig. 1(c)] the width of the interface increases due to the atomic mixing produced by each shear, and to the roughening of the interfaces; eventually a solid solution is formed.

Fourier analysis of the interface shows that, at moderate shearing frequencies [as in Fig. 1(a)], the smallest wave

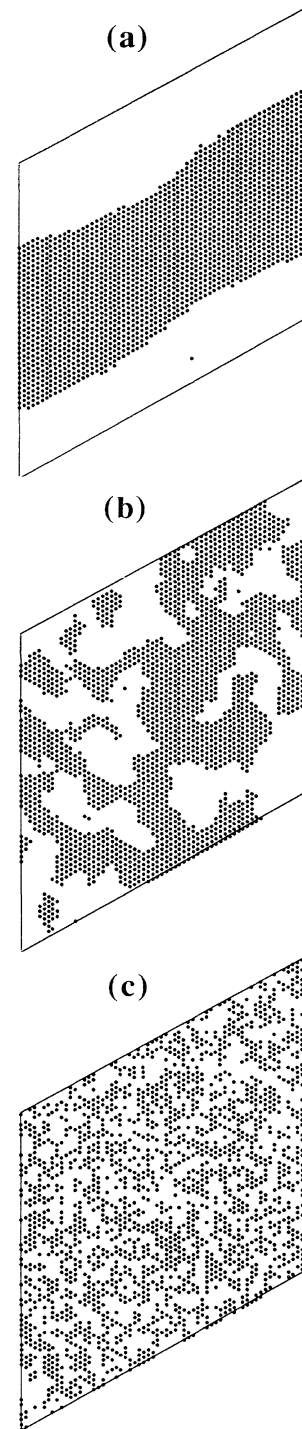


FIG. 1. Typical steady-state microstructures as observed in a (111) plane, for (a) $\gamma_{sh} = 1 \text{ s}^{-1}$, (b) $\gamma_{sh} = 10^{+3} \text{ s}^{-1}$, (c) $\gamma_{sh} = 10^{+5} \text{ s}^{-1}$; they were typically obtained after 250, 30 000, and 40 000 shears in (a), (b), and (c), respectively. In all cases the initial state was a bilayer of pure A and pure B , and the temperature was held constant at $T = 400$ K, $N = 64$.

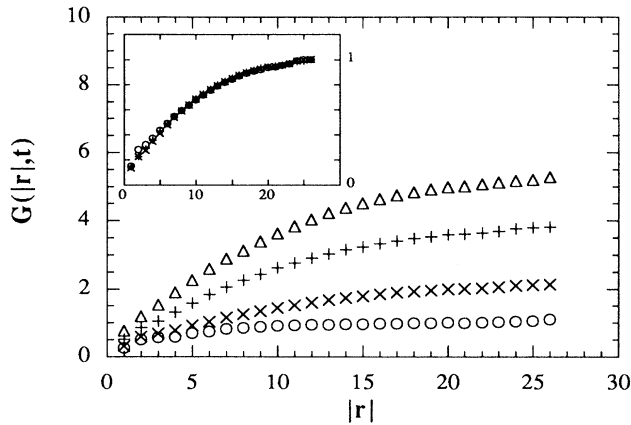


FIG. 2. Height-to-height correlation functions for $\gamma_{\text{sh}} = 100 \text{ s}^{-1}$ and $T = 273 \text{ K}$. \circ , \times , $+$, and Δ correspond to times 3.9×10^3 , 7.6×10^3 , 3.2×10^4 , and $6.2 \times 10^4 \text{ s}$, respectively. The inset shows the collapse of the last three curves when $G(r, t)/G(r_{\text{max}}, t)$ is plotted as a function of r ($r_{\text{max}} = N/\sqrt{6}$ due to the rhombohedral cell). G and r are given in units of a .

vector is most prominent. Furthermore, $G(|\mathbf{r}|)$ exhibits linear behavior at small values of $|\mathbf{r}|$, as shown in Fig. 2. Indeed, a sine wave leads to such a behavior, with the slope of $G(|\mathbf{r}|)$ being proportional to the amplitude of the wave. When the shearing rate is not too high [Fig. 1(a)], the amplitude of the wave grows and reaches a steady-state value. However, if the shearing rate is increased, waves of higher \mathbf{k} vector also become excited. This leads to the production of “fingers” of one phase protruding into the other, and eventually to a refinement of the microstructure, as seen in Fig. 1(b). Microstructures with wavy interfaces were indeed observed during ball milling experiments [6,7]. The degree of refinement can be measured by computing the first moment of the structure factor of atomic configuration, $S(|\mathbf{k}|)$, given by $S(|\mathbf{k}|) = \langle |N^{-3} \sum_i (n_i - 0.5) \exp(2\pi i \mathbf{k} \cdot \mathbf{r}_i)|^2 \rangle$ where n_i equals 1 or 0 depending if the site i at position \mathbf{r}_i is occupied or not by a B atom; the bracket denotes a spherical average over \mathbf{k} . It increases from $0.04a^{-1}$ for the initial configuration to $0.13a^{-1}$ at steady state for the conditions of Fig. 1(b). The same steady-state value is obtained by starting the simulations with the nearly solid solution of Fig. 1(c) and lowering the shearing rate to $\gamma_{\text{sh}} = 10^{+3} \text{ s}^{-1}$, while keeping $T = 400 \text{ K}$. This result indicates that there is only one stable steady state for the system. It is noteworthy that this steady state with a mesoscopic microstructure has no equivalent in the crystal at thermal equilibrium. Furthermore, the degree of refinement continuously increases on increasing γ_{sh} : no instability of the steady-state system towards a solid solution at a critical level of refinement is observed, which is contrary to predictions of models based purely on thermodynamics arguments [6,7].

Similar sequences have been obtained for temperatures ranging from 273 to 700 K. The only major difference

is that higher shearing frequencies are required at higher temperatures for stabilizing the same state: e.g., $T = 237 \text{ K}$ and $\gamma_{\text{sh}} = 1 \text{ s}^{-1}$ or $T = 400 \text{ K}$ and $\gamma_{\text{sh}} = 10^3 \text{ s}^{-1}$ [Fig. 1(b)] lead to microstructures with the same degree of refinement. Qualitatively, the same roughening and microstructure refinement as observed in Fig. 1 are obtained by fixing γ_{sh} and decreasing T .

We now propose an analytical model for studying the kinetic roughening of interfaces in crystals under shear. Existing models for kinetic roughening consider the case where the external forcing produces a microscopic perturbation of the interface (e.g., the landing and sticking of an atom onto a growing surface): this is not the case here since a single shearing results in a shift of a number of atoms, of the order of the interfacial area times the atomic interfacial density. Following Edwards and Wilkinson [8], we derive a Langevin-type equation for the case of system submitted to shearing frequencies that are moderate enough to maintain sharp interfaces and avoid overhang. Consider an $N \times N \times N$ simple cubic lattice of parameter a ($L = Na$) with periodic boundary conditions (the specific lattice is not relevant for the following); this crystal is submitted to shearing on $\{100\}$ planes which produce steps of height h at the interface. The height of the interface at position \mathbf{r} is defined by $Z_{\mathbf{r}}$ with $\mathbf{r} = (x, y)$ or equivalently by its Fourier transform $Z_{\mathbf{k}}$ with $\mathbf{k} = (k_x, k_y)$. We first compute the contribution from the shearing alone. Because of the random character of the shearing, the perturbation $\xi_{\mathbf{k}}$ added by one shear to the position of the interface has zero mean for all \mathbf{k} . A straightforward calculation shows that the only nonzero fluctuations are

$$\langle \xi_0 \xi_0 \rangle = (5/48)v^2 N^4, \quad (1a)$$

$$\langle \xi_{(k_x, 0)} \xi_{(-k_x, 0)} \rangle = v^2 N^2 / 4k_x^2 a^2, \quad (1b)$$

with an equation similar to Eq. (1b) for $\mathbf{k} = (0, k_y)$; v is the volume $v = ha^2$; the brackets denote ensemble averages over all possible shears. Equation (1) already points out two important results: (i) the average position of the interface [Eq. (1a) will exhibit large fluctuations, as indeed observed in the simulations], and (ii) the noise induced by a shear increases strongly at small \mathbf{k} .

For the relaxation, Wolf and Villain [17] have pointed out that in systems where interfacial fluxes are derived from chemical potentials the drift term should be proportional to $-M\nabla^4 Z_{\mathbf{r}}$, i.e., to $-Mk^4 Z_{\mathbf{k}}$ in Fourier space (with $k = |\mathbf{k}|$). M is the atomic mobility at the interface and is therefore proportional to the vacancy concentration C_v . We will assume that under moderate shearing intensities, the drift term has this same dependence. A last assumption is that the noise term arising from the thermal motion of the vacancy is negligible compared to the noise induced by the shears. This assumption was checked *a posteriori*, since its validity leads to height-to-height correlation functions that are proportional to $(\gamma_{\text{sh}}/M)^{1/2}$,

and this dependency was indeed observed in the simulations. The position of the interface is thus described by the following Langevin equation:

$$\partial Z_k / \partial t = -Mk^4 Z_k + \xi_k, \quad (2)$$

where ξ_k is given by Eq. (1). Simple models yield a power law dependence of C_v , and thus M , with γ_{sh} [15,16]; this could be implemented in Eq. (2). Since the exponents in such power laws are smaller than unity [16], keeping M constant, as done here and in the simulations, only shifts the values of γ_{sh} . From Eq. (2), it is seen that roughening of the interface is expected to first develop at vector $\mathbf{k}_{min} = 2\pi/L$, since it is the most affected by a shear and it undergoes the smallest recovery rate. From Eq. (2) the height-to-height correlation function $G(|\mathbf{r}|, t)$ can now be computed using the procedure of [8]: It is shown to be a linear function of $r = |\mathbf{r}|$ at small r values and to saturate at large r ; this is also observed in the simulations (see Fig. 2). Furthermore, calculation of the steady-state width of the interface σ (the rms of Z_r) yields $\sigma \propto (\gamma_{sh}/M)^{1/2} L^{5/2}$. The large roughness exponent found in this case, $\alpha = 5/2$, is a direct consequence of the macroscopic character of the perturbation introduced by a single shearing. After a transient regime $G(r, t)$ obeys an unusual but simple scaling: The data taken at different times collapse onto a single curve when $G(r, t)/G(r_{max}, t)$ is plotted as a function of r as shown in the inset of Fig. 2. In Fig. 3, the steady-state width of the interface obtained in the simulations is plotted as a function of L ; a power law provides a good fit of the data, but with an exponent $\alpha = 1.22 \pm 0.05$ rather than the predicted 2.5. We presently ascribe this discrepancy to (i) the partial trapping of vacancies at interfaces in the simulations [18], which results in a dependence of M with L when the bulk vacancy concentration is held constant, and (ii) the existence of some bulk diffusion, implying that a second recovery term proportional to $-k^2 Z_k$ may be required in Eq. (2). Both effects result in a slower growth of

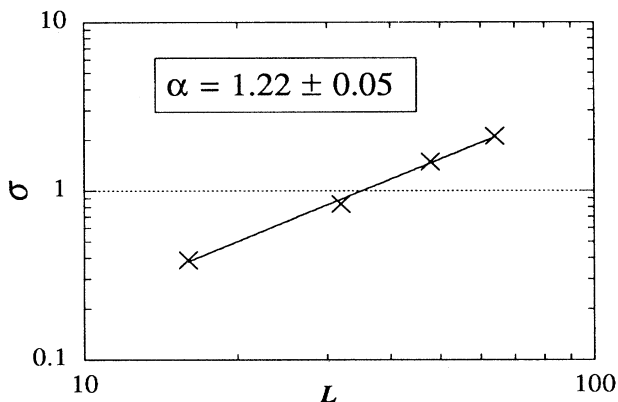


FIG. 3. Evolution of the steady-state width of the interface σ (in units of a) as a function of the system length L (in units of a); each point results from more than 500 independent measures; the solid line gives the best power law fit $\sigma \propto L^\alpha$.

the interface width with L . Further work is required to incorporate these effects in the model.

In conclusion, it is shown from simulations and analytical treatment that interfaces in crystals under shearing are expected to be rough. This nonequilibrium roughness induces a refinement of the microstructure, as observed experimentally. The kinetic approach introduced here provides a clear rationalization of ball milling experiments showing the formation of solid solution in systems with positive heat of mixing. The simulations suggest that a mesoscopic mixture of phases can exist at steady state at appropriate temperature and shearing rate.

Stimulating discussions with G. Martin, F. Haider, and T. Klassen are gratefully acknowledged. Thanks are due to T. Abinandanan for his permission to use and modify his Monte Carlo code for the present study. The research was supported by the U.S. Department of Energy, Basic Energy Sciences, Grant No. DEFG02-91ER45439.

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