Transient Ordered States in Phase-Separating Alloys

L. Reinhard and P. E. A. Turchi
Condensed Matter Division (L-268), Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California 94550

(Received 31 August 1993)

We demonstrate the existence of transient ordered phases in alloys which, at equilibrium, exhibit a definite tendency toward segregation. This is shown through a Monte Carlo study of the decomposition kinetics of a bcc TiV alloy based on first-principles electronic structure calculations. Specifically, we predict a transient $B32$ ordering of the quenched-in solid solution before separation into Ti- and V-rich disordered phases. We discuss the requirements for such unusual behavior in relation to experiment, and compare Monte Carlo results for a 2D model system with mean-field predictions.

PACS numbers: 71.45.Nt, 64.60.Cn, 64.60.My, 82.20.Wt

Despite substantial theoretical and experimental efforts, the kinetics of both ordering and segregation in alloys is still much less understood than the static aspects of phase stability. Quite often, one has to consider both phenomena simultaneously since in many systems of practical interest ordering and phase separation are not necessarily mutually exclusive processes. For example, precipitation of ordered intermetallics from a disordered matrix is widely used in alloy design to improve mechanical and physical properties. If, however, *all* product phases of a segregation reaction are disordered and possess the same crystal symmetry as the initial state, it is generally assumed that no ordering can occur and only atomic clustering takes place during the decomposition process.

Still, one can envisage a situation where an ordered phase is energetically stable (at $T=0$ K) with respect to the random alloy but has a higher ground state energy than the mixture of the pure elements. This ensures that at finite temperatures a part of the free energy curve of the ordered phase (typically for concentrations close to its stoichiometry) lies below the free energy for the random solid solution, but above the free energy of the equilibrium mixture of the disordered product phases. Since ordering involves diffusion on a much shorter length scale than decomposition, and is therefore much faster, a supersaturated solid solution can then lower its free energy by undergoing an ordering reaction, prior to the final decomposition into disordered equilibrium phases.

Guided by these arguments, Chen and Khachaturyan [1] have performed a numerical simulation of ordering-decomposition kinetics on a generic 2D square lattice assuming a pair interaction model. Their simulation technique is based on the mean-field microscopic kinetic theory:

$$\frac{dn(\mathbf{r},t)}{dt}=\sum_{\mathbf{r}'}L(\mathbf{r}-\mathbf{r}')\frac{\delta F}{\delta n(\mathbf{r}',t)} . \qquad (1)$$

Here, $n(\mathbf{r},t)$ is the site occupation and L the matrix of the kinetic coefficients. For the free energy F, the Bragg-Williams expression for the pairwise Ising Hamiltonian was employed. The results in Ref. [1] indicate that transient ordering may well occur during decomposition if the above-mentioned phase stability relationships are fulfilled by the underlying model Hamiltonian.

In this paper we investigate the temporal evolution of the microstructure of a specific binary bcc alloy, $\mathrm{Ti}_{0.5}\mathrm{V}_{0.5}$. We use the Monte Carlo kinetic Ising model [2], rather than the mean-field approach to describe this evolution. In contrast to Eq. (1), the Monte Carlo technique accounts for fluctuational nucleation, and we will discuss the resulting differences between the two descriptions below. The energetic parameters for $\mathrm{Ti}_{0.5}\mathrm{V}_{0.5}$ employed in our simulation were obtained with a first-principles electronic structure approach, namely, the generalized perturbation method (GPM) implemented within the Korringa-Kohn-Rostoker coherent-potential approximation (KKR-CPA) [3,4].

In the KKR-CPA-GPM, the formation energy ΔE_{form} of a particular chemical configuration $\{p_n\}$ ($p_n=1$ for a B atom on site n, 0 otherwise) in an $A_{1-c}B_c$ alloy is written as

$$\Delta E_{\mathrm{form}}(c)=\Delta E_{\mathrm{mix}}(c)+\Delta E_{\mathrm{ord}}(\{p_n\}) . \qquad (2)$$

Here, ΔE_{mix} is the energy of the random alloy (as specified by the CPA) with respect to the pure metals A and B. The ordering energy, ΔE_{ord}, is the difference in energy between any chemical configuration specified by $\{p_n\}$ and the random one and is given to the lowest order in perturbation by

$$\Delta E_{\mathrm{ord}}\approx\frac{1}{2}\sum_{n\neq m}V_{nm}(p_n-c)(p_m-c) , \qquad (3)$$

where $V_{nm}=V_{nm}^{AA}+V_{nm}^{BB}-2V_{nm}^{AB}$ represents an effective pair interaction between sites n and m.

For the $\mathrm{Ti}_{0.5}\mathrm{V}_{0.5}$ alloy, we have obtained the following values for the pair interactions (in mRy/atom) associated with the first seven coordination shells: $V_1=-0.27$, $V_2=1.05$, $V_3=-0.42$, $V_4=-0.34$, $V_5=-0.36$, $V_6=-0.1$, and $V_7=-0.01$ [4]. Using these interactions, we have calculated ordering energies for several alloy configurations, according to Eq. (3). Among the allowable configurations at equicomposition, the "coherently" phase-segregated state yields the lowest energy, ΔE_{seg}

0031-9007/93/72(1)/120(4)$06.00

© 1993 The American Physical Society

$=-1.6$ mRy/atom. Interestingly, the $B32$ superlattice has only a slightly higher ordering energy, $\Delta E_{B32}=-1.1$ mRy/atom [the $B32$ structure can be described as a sequence of two Ti planes and two V planes in the (111) direction]. Note that, because of the negative sign of their ordering energies, both the phase-segregated state and $B32$ are more stable than the random CPA medium. The competition between phase segregation and $B32$ can be adequately visualized in reciprocal space: The Fourier transform $V(\mathbf{k})$ of the pair interactions (see Fig. 1) exhibits minima at two special (Lifshitz) points: an absolute minimum at the origin and a local minimum at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ (in units of $2\pi/a$, where a is the bcc lattice parameter) which corresponds to the ordering wave vector of the $B32$ superlattice.

Monte Carlo simulations using the configuration-dependent Hamiltonian (3) with the above-mentioned set of interactions were performed in the canonical ensemble (Kawasaki dynamics) for the equiatomic composition with spin exchanges allowed only in the nearest-neighbor shell. A simulation box with its edges along threefold symmetry axes containing $32\times32\times33$ sites was employed with helical boundary conditions [2]. This box size is compatible with the $B32$ structure, and is big enough to minimize finite-size effects. Figure 2 shows a typical time evolution of the $B32$ long-range order (LRO) parameter η as well as of the Warren-Cowley short-range order (SRO) parameters α_1–α_3 after an instantaneous quench of the random alloy to inside the miscibility gap. The "anneal" temperature was 200 K, which corresponds to $T_s/2$, where T_s locates the top of the miscibility gap as obtained from the ordering part (3) of the GPM Hamiltonian *alone.* (Since we did not study global phase stability, i.e., did not consider the energy of mixing, the discrepancy with the experimentally determined $T_s=1123$ K [5] is not surprising.)

Immediately after the quench, one observes a fast buildup of SRO, compatible with the $B32$ local atomic order. Indeed, the SRO parameters α_2 and α_3 attain $\frac{1}{2}$ of their values for the fully ordered $B32$ structure ($\alpha_2=-1$, $\alpha_3=+1$) within 50 attempted Monte Carlo steps (MCS) per atom after the quench, whereas α_1 remains close to the $B32$ value of 0. After the first ~100 MCS the ordered $B32$ domains enter a "coarsening stage" during which the increase in local order slows down whereas the LRO parameter maintains its growth rate. At the maximum of the LRO parameter, visual inspection of the model crystal reveals a well-ordered $B32$ structure with occasional "defects," mostly antiphase boundary (APB) "segments," i.e., extra pieces of (111) planes occupied by A or B atoms. The subsequent phase separation leads to the disappearance of the ordered $B32$ structure and to the formation of A- and B-rich domains. Accordingly, the LRO parameter goes to zero and all SRO parameters become positive, indicating clustering.

The nucleation of the phase-segregated regions is "inhomogeneous" and starts mostly at "extended defects" created during the initial buildup of $B32$ order. Such defects are indeed effective in initiating segregation in an otherwise perfectly ordered structure; a single extra A plane, leading to a $BBAAABB$ sequence in the (111) direction, is sufficient to initiate segregation at $T=T_s/2$. However, a simulation at $T_s/2$ starting with a defect-free $B32$ structure reveals only fast initial relaxation to a partially ordered state, which then remains metastable without indication of phase separation up to at least 31 000 MCS. At higher temperatures, a perfectly ordered structure will eventually segregate, the faster the higher the temperature, because of the increasing formation of "thermal" defects, i.e., of A or B atoms which occupy the "wrong" sublattices and act as nucleation sites for separation. For example, the $B32$ "lifetime" is about 7000 MCS at $T=0.6T_s$.

In the late stage of the decomposition process, the

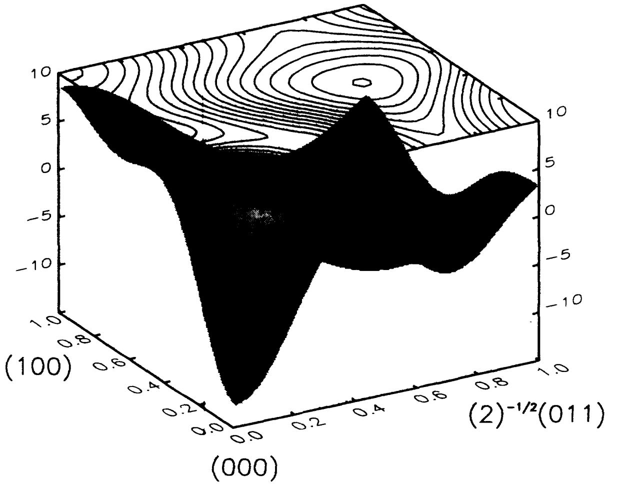

FIG. 1. Fourier transform $V(\mathbf{k})$ of the $Ti_{0.5}V_{0.5}$ GPM pair interactions in the (110) plane.

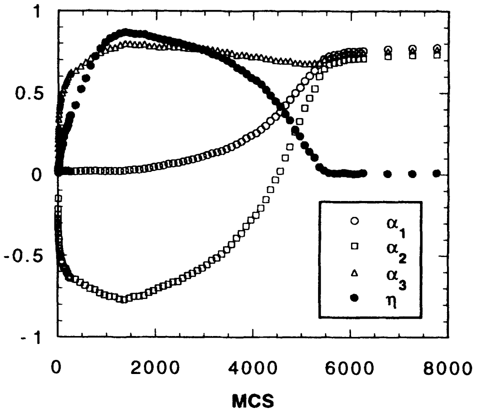

FIG. 2. Monte Carlo temporal evolution of SRO parameters α_1–α_3 and $B32$ LRO parameter η for $Ti_{0.5}V_{0.5}$, after an instantaneous quench to $T=\frac{1}{2}T_s$.

boundary between the A-rich and the B-rich regions is wet by the ordered phase. This can be seen in Fig. 3, where *two* consecutive (001) planes of the bcc model alloy, as obtained after 31 000 MCS, are displayed. In this projection, the $B32$ structure manifests itself as alternating rows of A and B atoms in (110) or $(\bar{1}10)$ directions, depending on the variants considered. In Fig. 3 the interface between the A-rich and the B-rich domains contains short segments of such rows indicative of $B32$-like local atomic arrangements at the phase boundary. As pointed out in Ref. [1], a stable ordered interface can be predicted from thermodynamics: Across the boundaries between the A- and B-rich phases the composition has to have intermediate values, for which the free energy of the ordered phase is lower than the free energy of the disordered solid solution.

Quite generally, within the pair interaction model the energetics needed for transient ordering necessitates a $V(\mathbf{k})$ with minima at $\mathbf{0}$ and the superlattice points $\mathbf{k}_{\mathrm{ord}}$ of the ordered structure. In the one-phase region above the miscibility gap one then has an absolute maximum of the diffuse scattering intensity $I(\mathbf{k})$ at $\mathbf{k}=\mathbf{0}$ and a local maximum of $I(\mathbf{k})$ at the superlattice ordering wave vectors, $\mathbf{k}=\mathbf{k}_{\mathrm{ord}}$, as can be seen, e.g., from the Krivoglaz-Clapp-Moss formula [6]. Therefore, when observed experimentally, such a signature of the diffuse scattering could indicate a possible transient ordering in the low temperature region.

We are not aware of any studies of chemical order in bcc Ti-V alloys. The experimental verification of the ordering-decomposition kinetics in this particular system might be difficult because of the intervening ω-phase transformation [7]. Also, the temperatures for which there is a substantial $B32$ ordering in our simulations might be too low for achieving sufficient diffusion rates. The latter difficulty could be overcome by alloying a third element to obtain a more negative ordering energy and therefore a higher metastable ordering temperature for $B32$. In general, ternary alloys offer a higher flexibility in tuning the interactions and the relative stability of various structures. For example, the addition of Fe could change the phase-separating character of Ti-V (transient $B32$ ordering investigated here notwithstanding) into a $B2$-like ordering tendency because both Fe-V and Fe-Ti exhibit an ordered $B2$ phase at equicomposition [4]. Thus, by fine tuning the concentration in Fe-Ti-V one could explore a region of near-degeneracy between phase segregation and a ternary equivalent of $B2$.

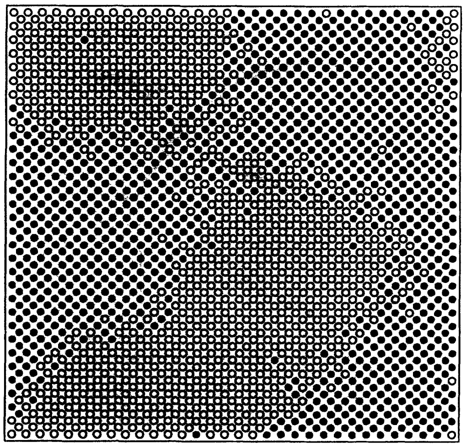

FIG. 3. Projection of two consecutive (001) planes of the $\mathrm{Ti}_{0.5}\mathrm{V}_{0.5}$ bcc model crystal, after 31 000 MCS at $T=\frac{1}{2}T_s$.

Recently, Chen *et al.* [8] have performed a diffuse x-ray scattering measurement on a single crystal of Au-19.1 at.% Fe quenched after a solution treatment at 973 K. The SRO intensity in their study exhibits an absolute maximum at (0,0,0) and a weak local maximum at $(1,\frac{1}{2},0)$. It is therefore conceivable that the Au-Fe system (possibly with ternary additions) could exhibit transient ordering in an appropriate domain of temperature and concentration. Interestingly enough, there exists a considerable controversy in the literature regarding the nature of the atomic arrangements in the Au-rich part of this system. Whereas some results indicate a $(1,\frac{1}{2},0)$ special point ordering [9] (similar to $\mathrm{Ni}_4\mathrm{Mo}$), other investigations seem to support the clustering hypothesis [8]. One then might speculate that these contradictory results are due to kinetic effects associated with a metastable $(1,\frac{1}{2},0)$ ordering followed by segregation, and time-resolved experiments are highly desirable.

Finally, in order to compare the Monte Carlo technique with the mean-field approach, we have performed simulations on a 2D square lattice using pair interactions from Ref. [1]. Several predictions of the mean-field model are confirmed. In particular, with both techniques, the interface between the disordered product phases remains ordered after thermal equilibrium has been reached, and the APBs play an important role in initiating separation. However, some differences are noteworthy. Most notably, the congruent order-disorder transition lines (Fig. 2 in Ref. [1]), which sharply delineate regions with distinctly different kinetic behaviors within the mean-field framework, cannot be located in our simulation. Instead we find a *gradual* change of the temporal evolution of the microstructure with concentration and anneal temperature. For "deep" quenches, i.e., well inside the two-phase region, phase separation starts primarily at "grown-in" APBs. For "shallow" quenches, closer to the miscibility line, segregation is mostly initiated by thermally activated defects. Similar differences between the Kawasaki dynamics and mean-field predictions have been reported for standard segregating systems: The mean-field spinodal can be located only in the limit of infinite interaction range [10], and only then the decomposition kinetics inside the spinodal can be adequately described by the mean-field kinetic theory [11] (in that case by the linearized Cahn-Hilliard equation).

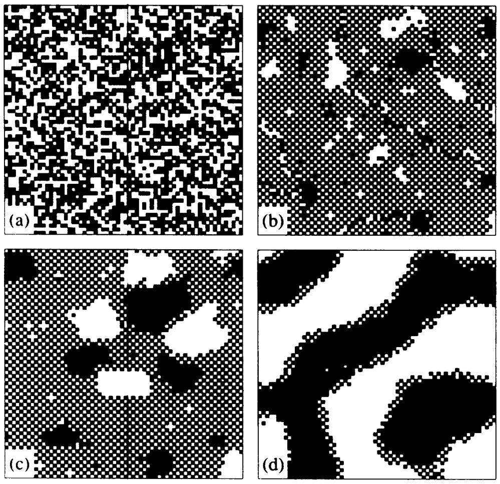

FIG. 4. Temporal evolution of a square lattice 2D model system with pair interactions from Ref. [1], after a quench to $T=\frac{1}{3}T_s$ (see text for a definition of T_s). (a) As-quenched random state. (b) After 240 MCS. (c) After 4700 MCS. (d) After 31 000 MCS.

Figure 4 shows the Monte Carlo temporal evolution of the microstructure of an equiatomic 2D system after a quench to $T=\frac{1}{3}T_s$, where $T_s \approx 0.21 V(\mathbf{k}=0)/k_B$, as obtained from our Monte Carlo simulation. A rapid ordering reaction leads to the formation of the "checkerboard" structure with occasional phase-segregated regions which are mostly located at APBs [Fig. 4(b)]. The concentration fluctuations along the APBs grow in extent [Fig. 4(c)] and lead to the final segregation into two disordered phases. This evolution differs somewhat from the predictions of Eq. (1) for quenches inside the ordering spinodal. In the mean-field case (see Fig. 5 in Ref. [1]) there are no concentration fluctuations in the disordered regions near the APBs. Instead, a homogeneous disordered phase grows at the expense of the ordered phase, the ordered phase then disorders, and at no time during the ordering-decomposition process do more than two phases appear. In contrast, the Monte Carlo simulations show a coexistence of three phases (A-rich disordered, B-rich disordered, and ordered) for intermediate times [see Fig. 4(c)]. This feature is also observed in our three-dimensional simulation for TiV. Conceivably, the homogeneous disordered phase found in the mean-field kinetics is due to the "ensemble averaging" effect inherent to Eq. (1). This averaging—exemplified by the continuous occupation variable $n(\mathbf{r},t) \in [0,1]$—tends to suppress concentration fluctuations, especially those not accompanied by spatial variations of the order parameter η.

In conclusion, our combined KKR-CPA-GPM and Monte Carlo study clearly shows the possibility of transient $B32$ ordering in $\mathrm{Ti}_{0.5}\mathrm{V}_{0.5}$. Similar kinetic behavior can be expected for other systems exhibiting an energetic competition between phase separation and ordering. The predictions of the microscopic mean-field diffusion equation are largely confirmed in a 2D Monte Carlo simulation, although the details of the microstructural evolution differ in the two approaches.

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

[1] L.-Q. Chen and A. G. Khachaturyan, Phys. Rev. B **44**, 4681 (1991).
[2] See, e.g., K. Binder and D. W. Heermann, in *Monte Carlo Simulations in Statistical Physics*, Springer Series in Solid State Sciences Vol. 80 (Springer, Berlin, 1988).
[3] P. E. A. Turchi *et al.*, Phys. Rev. Lett. **67**, 1779 (1991); **68**, 418(E) (1992).
[4] P. E. A. Turchi and M. Sluiter, Mater. Res. Symp. Proc. **253**, 227 (1992).
[5] *Binary Alloy Phase Diagrams*, edited by T. B. Massalski (American Society for Metals , Metals Park, OH, 1986), Vols. 1 and 2.
[6] M. A. Krivoglaz, in *Theory of X-Ray and Thermal Neutron Scattering by Real Crystals* (Plenum, New York, 1969); P. C. Clapp and S. C. Moss, Phys. Rev. **142**, 418 (1966).
[7] M. Ikeda *et al.*, J. Jpn. Inst. Met. **54**, 743 (1990).
[8] H. Chen *et al.*, Phys. Rev. B **42**, 2342 (1990).
[9] Y. Yoshida *et al.*, Phys. Rev. B **39**, 6395 (1989).
[10] D. W. Heermann, W. Klein, and D. Stauffer, Phys. Rev. Lett. **49**, 1262 (1982).
[11] D. W. Heermann, Z. Phys. B **61**, 311 (1985).

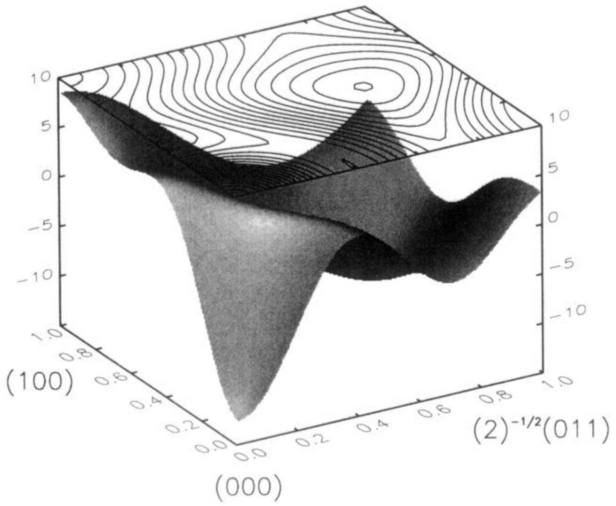

FIG. 1. Fourier transform $V(\mathbf{k})$ of the $Ti_{0.5}V_{0.5}$ GPM pair interactions in the (110) plane.

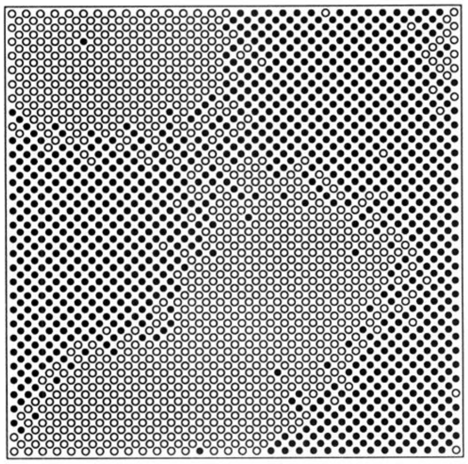

FIG. 3. Projection of two consecutive (001) planes of the $Ti_{0.5}V_{0.5}$ bcc model crystal, after 31 000 MCS at $T=\frac{1}{2}T_s$.

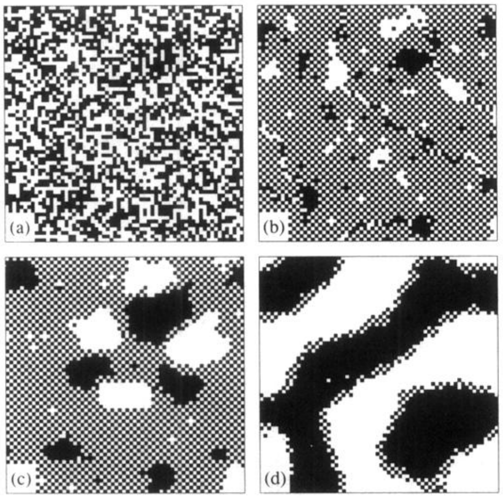

FIG. 4. Temporal evolution of a square lattice 2D model system with pair interactions from Ref. [1], after a quench to $T=\frac{1}{3}T_s$ (see text for a definition of T_s). (a) As-quenched random state. (b) After 240 MCS. (c) After 4700 MCS. (d) After 31 000 MCS.