Transient Ordered States during Relaxation from a Quenched Disordered State to an Equilibrium Disordered State

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We have investigated the kinetics of a ternary system using the cluster variation method and the path probability method in the pair approximation. From the calculated metastable phase diagram and kinetic path of the system, we demonstrated the existence of transient ordered states during the relaxation from the completely disordered state to the equilibrium disordered state due to the difference of relaxation time for the three species of atoms in ternary alloy. This suggests that it is possible to obtain an ordered state in a quenching process of ternary alloy in the disordered phase region of equilibrium phase diagram. [S0031-9007(97)04568-7]

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Nonequilibrium kinetics of materials plays an important role in materials growth. In recent years, new experimental methods such as rapid quenching, laser processing, ion beam bombardment, and various epitaxial processes have been used to prepare materials that are not in an equilibrium state thermodynamically. For the kinetics of order-disorder transformation [1–4] without phase separation, there are two usual processes. The one is the process that a disordered phase develops to an ordered phase for the kinetics of a quenched system from high temperature. The other is the process that an ordered phase relaxes to an equilibrium disordered phase which refers to annealing of a system. Generally in a quenching process the disordered configurations of a system in a high temperature are preserved (such as the quenching process to produce the amorphous state from the liquid state). It is generally believed that no ordering will occur when an alloy is quenched to a disordered phase region of an equilibrium phase diagram. However it is found that transient ordering can occur in quenching phase-separating alloys in a binary system [5,6]. In a ternary alloy, there are more time scales for different components to relax and a significant difference in the kinetics can arise.

In this Letter, we demonstrate the existence of a transient ordered phase in a ternary system in its kinetic process from the completely disordered state to the equilibrium disordered state and also some other features of the kinetics of the system. This suggests that it is possible to obtain an ordered state in a quenching process of the system in the disordered phase region of the equilibrium phase diagram. We describe a ternary system $A_xB_yC_{1-x-y}$ by the lattice gas with the Hamiltonian

$$\mathcal{H} = z \sum_{\{ij\}} \sum_{ss'} E_{ss'} c_i^s c_j^{s'} , \tag{1}$$

where z is the coordination number of the lattice. The variable $c_i^s = 1$ if the site i is occupied by an s $(= A, B, C)$ atom and is zero otherwise. The notation $\{ij\}$ means the summation over the pairs of nearest-neighbor lattice sites. $E_{ss'}$ represents the nearest-neighbor interaction energy. This Hamiltonian is equivalent to the spin-1 Blume-Emery-Griffiths (BEG) [7,8] Hamiltonian by mapping the spin $s_i = \{+1, -1, 0\}$ onto the species A, B, and C.

$$\mathcal{H} = J \sum_{\{i,j\}} s_i s_j - K \sum_{\{i,j\}} s_i^2 s_j^2 + L \sum_{\{i,j\}} (s_i^2 s_j + s_i s_j^2) . \tag{2}$$

The chemical potential terms are not included in Eq. (2). The energy parameters of the BEG Hamiltonian are related to the atomic nearest-neighbor interaction energies in the alloy Hamiltonian by the following equations [8]:

$$4J = E_{AA} + E_{BB} - 2E_{AB} , \tag{3}$$

$$\begin{aligned} 4K = {} & -E_{AA} - E_{BB} - 2E_{AB} - 4E_{CC} \\ & + 4(E_{AC} + E_{BC}) , \end{aligned} \tag{4}$$

$$4L = E_{AA} - E_{BB} + 2(E_{BC} - E_{AC}) . \tag{5}$$

The spin-1 BEG model is a model which originally was used to describe phase transition in ^{3}He-^{4}He mixtures [7] with a very rich phase diagram [9,10]. In the following we will show our results on a two-dimensional honeycomb lattice ($z = 3$) as a representative case. The results for the square lattice are similar. First we calculated the phase diagrams of the system by the cluster-variation method [11,12] in the pair approximation. In the pair approximation, the oriented-pair probability that an s atom on an α sublattice site is bonded to an s' atom on a β sublattice site is represented by $P_{ss'}$ and the probability that an s atom occupies an α sublattice site is represented by P_s^α. The symmetry of phase in the system is determined by the site probability P_s^α. We can also describe the phase by the magnetization and quadrupolar moments of the sublattices α and β in the BEG model.

$$\begin{aligned} m_\alpha &= \langle s_i \rangle_\alpha , \quad m_\beta = \langle s_i \rangle_\beta , \\ q_\alpha &= \langle s_i^2 \rangle_\alpha , \quad q_\beta = \langle s_i^2 \rangle_\beta . \end{aligned} \tag{6}$$

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The values of these parameters define the following phases with different symmetry: (1) the disordered phase: $m_\alpha = m_\beta$, $q_\alpha = q_\beta$; (2) the ordered phase O_1: $m_i \neq 0$, $m_\alpha \neq m_\beta$, the signs of m_α and m_β are contrary; and (3) the ordered phase O_2: $m_\alpha = 0$ or $m_\beta = 0$, $q_\alpha \neq q_\beta$.

Since the alloy Hamiltonian of Eq. (1) and the BEG Hamiltonian are equivalent, there are only three independent energy parameters such as J, K, L to describe the equilibrium phase diagram. There are six independent nearest-neighbor interaction energies. Therefore, there is no one by one correspondence between energy parameters J, K, L and nearest-neighbor interaction energy E_{ij}. We choose the interaction energies as $E_{AA} = E_{BB} = 1.0$, $E_{AB} = 0.8$, and $E_{AC} = E_{BC} = E_{CC} = 0.0$ which correspond to the energy parameters $J = 0.1$, $K = -0.9$, and $L = 0.0$. The system with such energy parameters is expected to exhibit no phase separation. Figure 1 shows the calculated equilibrium phase diagram of the system. The compositions of A and B atoms are taken to be the same (x_1, x_2, and x_3 are used to describe the compositions of components A, B, and C, respectively). In the phase diagram, there are two ordered phases O_1 and O_2. In the ordered phase O_1, component C is disorderly distributed and the ordering occurs between A and B atoms which reflects the usual binary ordering scenario of A and B atoms. In the ordered phase O_2, the ordering occurs between components C and $A + B$. Between the ordered phase O_1 and the ordered phase O_2, there is a V-shape disordered region. Our calculated equilibrium phase diagram agrees well with the previous results on the same system [4,13,14].

In the following, we consider the kinetics of the system. Two factors affect the kinetics of the system: (1) the atomic interaction energy and (2) the activation barrier height. Generally the activation barrier energies of A and B atoms are different. First we analyze an extreme case, i.e., A atoms move much slower than B and C atoms. The initial state of the system is chosen to be in a highly disordered state, for example, quenched from high temperature. The system will relax to its equilibrium state in two stages. In the first stage, only B and C atoms move while A atoms are in a state of relative rest because A atoms move much slower than B and C atoms. The system evolves to a metastable state in which A atoms remain in their disordered configuration and B and C atoms have relaxed to their local equilibrium state. After the system reaches the metastable state, the evolution process enters its second stage. In the second stage, A atoms slowly move and the whole system relaxes to its final equilibrium state gradually.

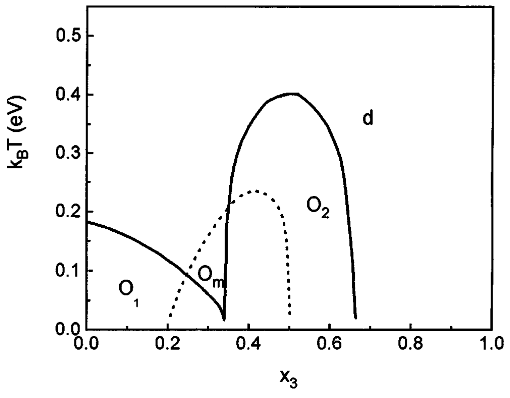

FIG. 1. Calculated equilibrium phase diagram (solid line) and metastable phase diagram (dotted line) at stoichiometry $x_1/x_2 = 1$ with the energy parameters $E_{AB} = 0.8$ eV, $E_{AA} = E_{BB} = 1.0$ eV. k_B is the Boltzmann constant. O_1 and O_2 are two ordered phases in the equilibrium phase diagram and O_m is the ordered phase in the metastable phase diagram. The disordered phase is indicated as d.

We have calculated the metastable phase diagram of the system. In the calculation, we used the modified Kikuchi approximation [15] in order to study the metastable phase. Since A atoms are randomly distributed in the metastable state, there are thus three constraint equations to represent the random distribution of A atoms.

$$\sum_s P_{As} = x_1, \qquad \sum_s P_{sA} = x_1, \qquad P_{AA} = x_1^2 . \qquad (7)$$

The dotted line in Fig. 1 is the calculated metastable phase diagram. It is interesting to note that the ordered phase region of the metastable phase diagram is not all included in the ordered phase region of the equilibrium phase diagram. Some of the metastable ordered phase region overlaps with the equilibrium disordered phase region. It means that a transient ordered phase O_m will occur in the first stage of kinetic evolution of a highly disordered phase in the overlapping region if A atoms move much slower. Since the equilibrium phase of this overlapping region is the disordered phase, this transient ordered phase will evolve to an equilibrium disordered phase finally. Therefore its kinetic route is expected to be disordered state-ordered state-disordered state. From Fig. 1 it can be seen that the region of the metastable phase O_m also overlaps with that of the ordered phases O_1 and O_2. In the overlapping regions between the metastable phase O_m with the ordered phases O_1 and O_2, we also expect that a transient ordered state characteristic of O_m occurs during the relaxation from the initial disordered phase to the ordered phases O_1 and O_2 if A atoms move slower.

We employ the path probability method (PPM) [1,2] to investigate the nonequilibrium evolution process. The path probability method can be shown to be equivalent [16] to the master equation method [17] in the pair approximation. In the kinetic process, there are two atom movement mechanisms: (1) the direct interchange of an atom with a nearest-neighbor atom (atom-atom interchange) and (2) the interchange of an atom with an adjacent vacancy (vacancy mechanism). A general case will combine both two atom movement mechanisms. We consider a representative kinetic mechanism which allows only the interchanges between components A and B with component C. This mechanism is used in the following two systems: (1) a conventional ternary alloy with a direct atom interchange mechanism with the condition that the A-B atom interchange is much slower than other atom interchanges and (2) a quasiternary system with two atomic constituents and one vacancy component with an atom-vacancy interchange mechanism. We are concerned with the case of the full range of vacancy concentration which can describe the ordering and disordering of the codeposition monolayer of two atomic constituents onto a crystal surface [4] rather than the kinetics of bulk binary alloys mediated by a very small vacancy concentration. Other kinetic mechanisms can lead to a quantitative difference in the kinetics of the system but quantitative features will remain.

In order to investigate its kinetic behavior we have used the PPM in the pair approximation. There are six independent pair probabilities which are characterized by three long-range order (LRO) parameters

$$\gamma_1 = P_A^{\alpha} - P_A^{\beta}, \qquad \gamma_2 = P_B^{\alpha} - P_B^{\beta}, \qquad \gamma_3 = P_{AC} - P_{CA}, \tag{8}$$

and three short-range order (SRO) parameters

$$\gamma_4 = P_{AC} + P_{CA}, \qquad \gamma_5 = P_{BC} + P_{CB}, \qquad \gamma_6 = P_{AB} + P_{BA}. \tag{9}$$

The LRO parameters γ_1 and γ_2 have opposite signs in the ordered phase O_1. In phase O_2, these LRO parameters have the same sign. In the disordered phase all the LRO parameters are zero.

The pair approximation of the PPM leads to a set of six coupled nonlinear differential equations which has the form

$$\frac{d}{dt}\gamma_i(t) = f_i(\tau_A, \tau_B, \gamma_1, \gamma_2, \gamma_3, \gamma_4, \gamma_5, \gamma_6), \tag{10}$$

where

$$\tau_A = \tau_{AC} \exp\left(-\frac{z(E_{AC} - E_{CC})}{k_B T}\right), \tag{11}$$

$$\tau_B = \tau_{BC} \exp\left(-\frac{z(E_{BC} - E_{CC})}{k_B T}\right). \tag{12}$$

τ_{AC}^{-1} is the diffusive rate for A atoms and component C (C atoms for direct interchange or vacancies for vacancy interchange). τ_{BC}^{-1} is the diffusive rate for B atoms and component C. τ_A and τ_B are the time scales for the relaxation of A and B atoms, respectively. When E_{AC}, E_{BC}, and E_{CC} are taken to be zero, $\tau_A = \tau_{AC}$ and $\tau_B = \tau_{BC}$. Because τ_A and τ_B depend on E_{AC}, E_{BC}, and E_{CC}, even in the case $\tau_{AC} = \tau_{BC}$, τ_A and τ_B could be much different if E_{AC} and E_{BC} are much different. Different sets of $E_{ss'}$ with the same J, K, L lead to the same equilibrium phase diagram. From Eq. (10), they give only different time scales τ_A and τ_B. The other factors in Eq. (10) depend only on J, K, L. Therefore, the interaction energy $E_{ss'}$ affects the kinetics of the system only through the energy parameters J, K, L and the time scales τ_A and τ_B.

We have made the calculation on the kinetics of the system in the overlapping region between the equilibrium disorder phase (d) and the metastable ordered phase O_m in Fig. 1. The initial state is chosen as a completely random state which can be obtained by quenching the system from high temperature. Thus the initial values of the SRO parameters are those characteristic of a completely random state. The LRO parameters are set to 10^{-6} at $t = 0$ to describe the incipient fluctuation. The differential equations describing the kinetics of the system were integrated numerically using Gear's method [18] appropriate to stiff differential equations. The equilibrium values obtained from the kinetic equations at a sufficiently long time reproduced those obtained from the phase diagram calculation.

Figure 2 illustrates the evolution of the LRO parameter at a typical point in the overlapping region. We have taken $\tau_A/\tau_B = 10^3$. There are two types of transient ordered state. One (denoted by symbol O_{t1}) has the characteristic of the metastable phase O_m in the metastable phase diagram of Fig. 1. The other (denoted by symbol O_{t2}) has the characteristic of O_1 because its LRO parameters γ_1 and γ_2 have the opposite sign. It shows that the kinetics of the system is more complicated than that from the mere analysis of the metastable phase diagram. The system first evolves to the transient ordered state O_{t1} characteristic of O_m in which γ_1 is zero and A atoms remain disordered. After that, γ_1 becomes nonzero gradually and has the opposite sign of γ_2 while the absolute value of γ_2

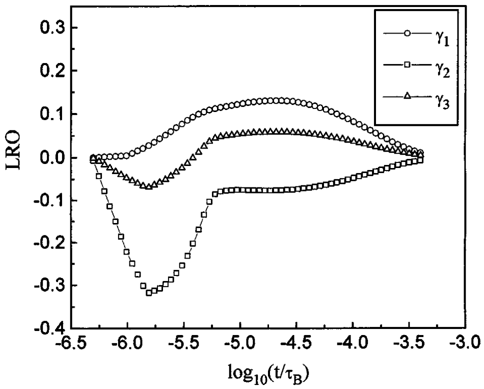

FIG. 2. Evolution of the LRO at a typical point in the overlapping region between the equilibrium disordered phase and the metastable ordered phase O_m with the compositions of three components $x_1 = 0.35$, $x_2 = 0.35$, and $x_3 = 0.3$. $k_B T = 0.1$ eV and $\tau_A/\tau_B = 10^3$.

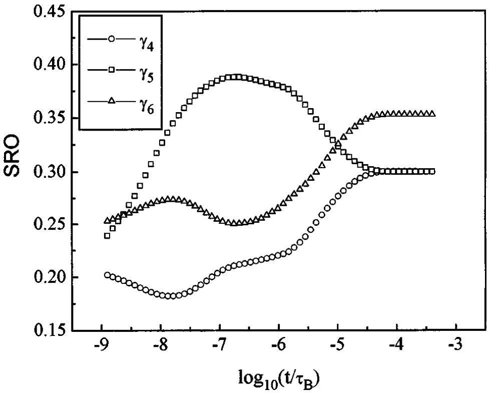

FIG. 3. Evolution of the SRO at a typical point in the overlapping region between the equilibrium disordered phase and the metastable ordered phase O_m with the compositions $x_1 = 0.35$, $x_2 = 0.35$, and $x_3 = 0.3$. $k_B T = 0.1$ eV and $\tau_A/\tau_B = 10^3$.

becomes smaller and γ_3 changes from a negative value to a positive one. Finally all the LRO parameters become zero. We could consider the kinetics in the overlapping region as a competition between O_1 and O_2 since it is in the V-shape region between O_1 and O_2.

Figure 3 shows the evolution of the SRO at the same parameter point as that of Fig. 2. From the time scale in the figure, we can see that all the SRO parameters change very rapidly. There are several stages of the change. They first develop from the values of the completely disordered state into that of the correlated state with short-range order until the system begins to develop into the transient phase O_{t1}. Then the SRO parameters evolve to the quasiequilibrium values of the transient phase O_{t1} and then that of O_{t2}. Finally, all the SRO parameters develop to their equilibrium values, and then remain almost constant during the time period when the LRO decays to zero of its final equilibrium disordered phase. This final stage of kinetics shows that the system here is driven to its equilibrium disordered state by entropy alone since the SRO parameters change very little, which has the same characteristic with other disordering kinetics [2–4].

We have also investigated how kinetics of the system changes with the ratio τ_A/τ_B. Smith and Zangwill [4] have studied the kinetics of ordering and disordering on a two-dimensional honeycomb lattice by the master equation method. They have considered only the case $\tau_A/\tau_B = 1$ which shows no transient state. In our study, we find that when $\tau_A/\tau_B = 1$, the initial completely random state will always relax to the equilibrium disordered state directly and no transient ordered state occurs. With the increase of ratio τ_A/τ_B, we find that the ordering parameters of the transient ordered state increase gradually. Therefore $\tau_A/\tau_B \neq 1$ is the necessary condition for the occurrence of the transient ordered state O_{t1}. The kinetics in the other regions of the phase diagram also shows that more than one type of transient ordered state can occur along the kinetic path [19].

In conclusion, we have investigated the kinetics of a ternary system. From the calculation of the metastable phase diagram, we have predicted the occurrence of a transient ordered state O_m in the kinetic process of the system in the region of the metastable phase O_m if one of three components has a slower relaxation time. Since the calculation of the metastable phase diagram has no relation to the kinetic mechanism, the occurrence of the ordered state O_m in the kinetics of the system does not depend on the specific kinetic mechanism. We have calculated the evolution of the LRO and SRO using PPM in the pair approximation. We find that there are two transient ordered states O_{t1} and O_{t2} in a relaxation from the completely disordered state to the equilibrium disordered state in some composition region. When we quench the transient ordered state O_{t1} or O_{t2} in the disordered region of the phase diagram, we can preserve an ordered state in a temperature at which otherwise an equilibrium disordered phase should occur.

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