Monte Carlo Study of Ordering Processes in fcc-Based Ni-Mo Alloys

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The Monte Carlo simulations were carried out to clarify the ordering mechanisms in fcc-based Ni-Mo alloys of Ni₄Mo, Ni₃Mo and Ni₂Mo. When the pairwise atomic interactions up to the eighth coordinate shells are taken into account, the simulation results are consistent with the experimental changes in electron diffraction pattern during the ordering processes in Ni₄Mo, Ni₃Mo and Ni₂Mo alloys. In the early stage of ordering, subunit cell clusters of D1_a, D0₂₂ and Pt₂Mo structures are first generated to form the short range ordered (SRO) state. The selective growth of stable D1_a and/or Pt₂Mo-type ordered domains is involved in the transition to the long range ordered (LRO) state in the following stage.

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I. Introduction

Order-disorder phenomena of diffusional phase transformations are observed in many kinds of binary alloys. Ni-rich Ni-Mo alloys quenched from the disordered fcc (A1) region transform into two types of long range order (LRO) structures with annealing: one is D1_a structure of A₄B-type, and the other is Pt₂Mo of A₂B-type. The projected structures of LRO are shown in Figs. 1(a) and (b). Both structures are formed by periodic insertion of (420)_{fcc} planes of Mo into the Ni-matrix. The spacings of Mo-planes in D1_a and Pt₂Mo structures are five times and three times of the (420)_{fcc} spacings, respectively. Thus, corresponding superlattice reflections appear at {4/5 2/5 0} positions for D1_a structure and {4/3 2/3 0} for Pt₂Mo in the diffraction patterns, where {hkl} denotes hkl and its equivalent positions in terms of the fundamental fcc lattice. The ordering reactions from A1 to D1_a and/or Pt₂Mo are known to exhibit remarkable characteristics. Figure 2 shows time-evolution of (001) electron diffraction patterns in Ni₄Mo (left column) and Ni₃Mo (right column) at 873 K. After long-time annealing (Fig. 2(d)), Ni₄Mo exhibits superlattice reflections at {4/5 2/5 0}, while Ni₃Mo gives intensity maxima at {4/5 2/5 0} and {4/3 2/3 0}. The D1_a-ordering of

Fig. 1 [001] projection of ordered structures which are considered to appear in the fcc-based Ni-Mo system, (a) D1_a, (b) Pt₂Mo, (c) D0₂₂ and (d) N₂M₂. Closed and open circles denote the Mo and Ni columns, and large and small ones indicate $z=0$ and $z=1/2$ planes, respectively.

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Fig. 2 (001) electron diffraction patterns of Ni_4Mo (left column) and Ni_3Mo alloys (right column), (a) as-quenched from 1273 K (1423 K for Ni_3Mo), and annealed at 873 K for (b) 7.2, (c) 86.4 and (d) 172.8 ks.

LRO prevails in the former alloy, while two-phase mixture of D1_a and Pt_2Mo structures appears in the later. On the other hand, the as-quenched states of both alloys (Fig. 2(a)) show diffuse intensity maxima at $\{1 \ 1/2 \ 0\}$ positions due to short range order (SRO). The maxima in the SRO states do not coincide with those in the LRO states for the Ni–Mo system.

The ordering processes in the fcc-based Ni–Mo alloys have been intensively investigated by many researchers so far^{(1)–(11)}. Some ordered structures, *e.g.* D0_{22} ⁽³⁾⁽⁸⁾⁽¹¹⁾ and N_2M_2 ⁽⁹⁾⁽¹⁰⁾ illustrated in Figs. 1(c) and (d) respectively, were considered to be primary structures in the SRO state, since they exhibit superlattice reflections at $\{1 \ 1/2 \ 0\}$. However, details of the SRO structure in real space and of their changes during ordering processes are still left unclear. This is due to the difficulty in determination of the atomic arrangements in the SRO states. In high resolution transmission electron microscopy

(HRTEM), for example, one can observe atomic arrangements projected along the incident beam direction. Various local configurations of atoms are inevitably superimposed in an HRTEM image of SRO. Several experimental factors, such as foil thickness, defocus and top-bottom effect, also govern the HRTEM image contrasts⁽¹²⁾⁽¹³⁾. Therefore, the interpretation of the image contrast for the SRO states are not so simple.

To overcome the experimental difficulties, we carried out Monte Carlo simulation of the ordering process in Ni_4Mo ^{(14)–(16)} in a previous study. The simulation represented successfully the experimental results of electron diffraction and HRTEM of Ni_4Mo when appropriate values of the pairwise atomic interactions are assumed. We also analyzed the changes in local atom configuration during the ordering process in Ni_4Mo . In the present study, the Monte Carlo simulation of ordering processes is extended to a non-stoichiometric composition range between 20.0 at% Mo (Ni_4Mo) and 33.3 at% Mo (Ni_2Mo). We will discuss the effect of Mo content on the ordering processes in the Ni–Mo system.

II. Model and Simulation

Let us consider an A_{1-x}B_x ($0.200 \leq x \leq 0.333$) alloy system consisting of $20 \times 20 \times 20$ fcc unit cells with the periodic boundary conditions. The internal energy of the system, E , is assumed to be given by summation of the pairwise interaction energy as

$$E = - \sum_n V(n) \left\{ \sum_{\langle n\text{NN} \rangle} \sigma_i \sigma_j \right\}, \quad (1)$$

where σ is the site-occupation operator defined as $\sigma_A = +1$ and $\sigma_B = -1$, and $\langle n\text{NN} \rangle$ denotes summation over the n -th nearest neighbor pairs. The pairwise interaction parameter of the n -th nearest neighbor atoms $V(n)$ is given by

$$V(n) = E_{AB}(n) - \frac{1}{2} \{ E_{AA}(n) + E_{BB}(n) \}, \quad (2)$$

where $E_{AB}(n)$, $E_{AA}(n)$ and $E_{BB}(n)$ are the bonding energy of A–B, A–A and B–B atom pairs, respectively. If the value of $V(n)$ is positive, the system prefers like-atom pairs, and unlike-atom pairs if it is negative.

In the Monte Carlo simulations, A and B atoms are first distributed randomly on the lattice sites, and nearest neighbor atoms chosen at random are exchanged with each other, according to the Kawasaki spin-flip dynamics⁽¹⁷⁾. The exchanging probability for a pair of nearest neighboring atoms is given by

$$W(\Delta E, T) = \frac{1}{2} \left[1 - \tanh \left(\frac{\Delta E}{2k_B T} \right) \right], \quad (3)$$

where ΔE is the energy gain caused by the exchange, and k_B and T are Boltzmann's constant and the absolute temperature, respectively. If the value of $W(\Delta E, T)$ is larger than a shuffled random number between 0 and 1, the neighboring atoms are exchanged. The time for atom-

ic exchange is measured in units of Monte Carlo step (MCS); one MCS corresponds to $32000 (20 \times 20 \times 20 \times 4)$ attempts to exchange neighboring atoms, namely one attempt of exchanging per one atom.

The positions of the neighboring sites on the fcc lattice are illustrated in Fig. 3. The values for the interaction parameters were determined in the almost same way as described previously⁽¹⁵⁾: We first determined the ranges of the parameters which can produce $D1_a$ and/or Pt_2Mo structures as the ground state in the composition range between A_4B and A_2B ⁽¹⁸⁾⁽¹⁹⁾. The values of the parameters were optimized within the ranges so that the simulation results could reproduce well the experimental ones of electron diffraction, HRTEM and X-ray diffraction⁽¹⁵⁾⁽²⁰⁾. The evaluated values of $V(n)$ in the present work are listed in Table 1. We reported that the interaction parameters up to the fifth nearest neighbors (NN) are necessary to describe the ordering of $D1_a$ in Ni_4Mo . However, we found that the parameters up to the eighth NN must be taken into account to reproduce the ordering processes for the wide composition range. Microdomains of $D1_a$ and Pt_2Mo structures cannot grow into LRO domains at A_3B composition without the eighth NN interactions $V(8)$. The effect of $V(8)$ will be discussed in Section III-3. The temperature T is set to be about two-third of the critical temperature of $D1_a$ structure given by Bragg-Williams' approximation.

Fig. 3 Positions of neighboring sites on the fcc lattice. Spheres with number n in the figure are the n -th nearest neighbors for the black sphere on the corner of the lattice.

Table 1 Pairwise atomic interaction parameters $V(n)$'s used in the simulations.

Composition	A_4B	A_3B and A_2B
$V(1)$	<0	<0
$V(2)/ V(1) $	0.2	0.4
$V(3)/ V(1) $	0.1	0.1
$V(4)/ V(1) $	-0.4	-0.4
$V(5)/ V(1) $	0.1	0.1
$V(6)/ V(1) $	0	0.15
$V(7)/ V(1) $	0	0.01
$V(8)/ V(1) $	0	-0.05
$k_B T/ V(1) $	1.0	1.0

III. Results and Discussion

1. Fourier power spectra

Figure 4 shows time-evolution of (001) Fourier power spectra of atomic arrangements obtained by the Monte Carlo simulations at A_4B (left), A_3B (center) and A_2B (right) compositions. In the early stage of ordering (Fig. 4(a)), the intensity maxima at $\{1 \ 1/2 \ 0\}$ positions are obtained at all the compositions. Ring-shaped diffuse scatterings through $\{1 \ 1/2 \ 0\}$ and $\{2/3 \ 2/3 \ 0\}$ positions become stronger with increasing B-concentration. With the progress of ordering, distinct intensity maxima appear at $\{4/5 \ 2/5 \ 0\}$ positions of $D1_a$ for A_4B and $\{2/3 \ 2/3 \ 0\}$ of Pt_2Mo for A_2B . These two types of maxima are simultaneously observed for A_3B , indicating two phase mixture of $D1_a$ and Pt_2Mo . One can see that the superlattice reflections at $\{2/3 \ 2/3 \ 0\}$ positions of Pt_2Mo structure are elongated along one of the $\langle 110 \rangle$ directions, as observed in Fig. 2. The time-evolution of the spectra are in quite good agreement with the experimental results of Ni_4Mo and Ni_3Mo shown in Fig. 2 and that for Ni_2Mo reported by Kulkarni *et al.*⁽²¹⁾ Thus, the ordering processes in the fcc-based Ni-Mo system can be explained in terms of the pairwise atomic interactions.

Fig. 4 Temporal change of (001) Fourier power spectra of atomic arrangements during the ordering processes for A_4B (left column), A_3B (center column) and A_2B compositions (right column), obtained with the parameters given in Table 1. Each spectrum is illustrated in appropriate five grey levels. Simulation time from (a) to (d) are 20, 50, 500, 3000 Monte Carlo steps (MCS) for A_4B , 40, 200, 700, 3000 MCS for A_3B , and 20, 100, 600, 3000 MCS for A_2B , respectively.

2. Atomic arrangements

Figure 5 demonstrates (001) cross-sectional views of temporal evolution of atomic arrangements in A_4B , A_3B and A_2B alloys. For the case of A_4B composition, sub-unit cell clusters of $D1_a$ (marked A), $D0_{22}$ (marked B) and Pt_2Mo structures (marked C) are formed in the early stage of ordering, as seen in Figs. 5(a) and (b). The mixed

state of the clusters synthesizes static concentration waves corresponding to the $\{1\ 1/2\ 0\}$ diffraction intensity maxima in the SRO state⁽¹⁴⁾⁻⁽¹⁶⁾. In the late stage, however, most $D0_{22}$ and Pt_2Mo -type clusters disappear and $D1_a$ -type domains grow preferentially as seen in Figs. 5(c) and (d). One-dimensional arrays of B atoms along the $[100]$ or $[010]$ directions marked D appear in $D1_a$ -domains with c -axes parallel to the (001) plane.

Fig. 5 (001) cross sectional views of atomic arrangements for A_4B , A_3B and A_2B compositions, at (a) 10, (b) 100, (c) 500 and (d) 3000 MCS.

Subunit cell clusters of $D1_a$, $D0_{22}$ and Pt_2Mo structures are also formed in the early stage of ordering for A_3B composition. The formation of N_2M_2 -type ordered structure⁽¹⁰⁾, shown in Fig. 1(d), is forbidden. One can see that the fraction of Pt_2Mo -type among the subunit cells are larger than those for A_4B composition. The increase of Pt_2Mo subunit cells intensifies ring-shaped diffuse scatterings in the Fourier spectra of Fig. 4. In the case of A_3B composition, Pt_2Mo and $D1_a$ -type domains develop at the same time as seen in Figs. 5(c) and (d).

For A_2B composition, the fractions of Pt_2Mo and $D0_{22}$ -type are large, as seen in Figs. 5(a) and (b). In addition, small segments of N_2M_2 structure are locally formed in regions enriched in B-atoms as marked E. Only Pt_2Mo -type domains can develop and remain in the late stage in Figs. 5(c) and (d). The regions marked F are Pt_2Mo -domains with c -axes parallel to the (001) plane.

One can see that [001] projected Pt_2Mo -domains have a parallelogram-shaped morphology with long diagonals along one of the $\langle 110 \rangle$ directions. This morphology leads the elongation of Pt_2Mo superlattice spots toward [110] or $[\bar{1}10]$ directions in the (001) diffraction patterns. Two types of Pt_2Mo -domains with long diagonals along one of $\langle 110 \rangle$ are illustrated in Fig. 6. In the case of Fig. 6(a), the long diagonal of the Pt_2Mo -domain is parallel to like-atom arrays along [110], while it is perpendicular to the arrays in Fig. 6(b). Schematic diffraction patterns from the two type of domains are given at the bottom. The shape of Pt_2Mo superlattice spots recognized in Fig. 4 corresponds to Fig. 6(b)-type. It indicates that like-atom arrays parallel to $\langle 110 \rangle$ are difficult to form, since the Pt_2Mo domain in Fig. 6(a) contains longer like-atom arrays along [110] than in Fig. 6(b). The preferential growth of Fig. 6(b)-type domains results from the ordering tendency along $\langle 110 \rangle$ directions due to the negative values of $V(1)$ and $V(4)$.

3. Ordering processes in the fcc-based Ni-Mo system

The results of the Monte Carlo simulations indicate that the ordering process in the fcc-based Ni-Mo system can be divided into two steps. The first step ($A1 \rightarrow SRO$) is the formation of subunit cell clusters of $D1_a$, $D0_{22}$ and Pt_2Mo structures, and the second one ($SRO \rightarrow LRO$) is development of $D1_a$ and/or Pt_2Mo -domains. These two steps are explained in terms of atomic pair-correlations, as follows. Figure 7 shows the values of Warren-Cowley parameters $\alpha(n)$'s for the relevant ordered structures shown in Fig. 1. The parameter $\alpha(n)$ is defined⁽²²⁾ as

$$\alpha(n) = 1 - P_{BA}(n)/x, \quad (4)$$

where $P_{BA}(n)$ is the probability of finding a B-atom at a lattice point in the n -th coordinate shell centered on an A-atom, and x is the atomic fraction of B-atom. The parameter $\alpha(n)$ takes a positive value if the number of like-atom pairs (clustering tendency) of the n -th nearest neighbors is larger than that in the completely disordered state, while it turns negative if unlike-atom pairs (ordering tendency) is dominant. One can see in Fig. 7 that the relevant structures, $D1_a$, $D0_{22}$, Pt_2Mo and N_2M_2 , have

Fig. 6 Shapes of Pt_2Mo -domains (upper) and their diffraction patterns (bottom), (a) and (b) illustrate Pt_2Mo -domains with the longer and shorter diagonals parallel to like-atom arrays along the [110] direction, respectively.

the similar tendencies of $\alpha(n)$'s up to the fourth coordinate shells except for $\alpha(4)$ of $D0_{22}$,

$$\alpha(1), \alpha(4) \leq 0, \quad (4)$$

$$\alpha(2), \alpha(3) \geq 0. \quad (5)$$

Subunit cells of $D1_a$, $D0_{22}$, Pt_2Mo and N_2M_2 structures are therefore expected to appear in the SRO states of the Ni-Mo system. However, the formation of N_2M_2 structure of AB-type requires local enrichment in B-atom in the matrix, and then the probability of the formation of N_2M_2 structure becomes considerably low. Accordingly, the SRO state involve a mixed state of subunit cell clusters of $D1_a$, $D0_{22}$ and Pt_2Mo structures in the early stage of ordering.

It is noted that the values of $\alpha(8)$ for $D0_{22}$ and N_2M_2 structures are unity, while $D1_a$ and Pt_2Mo have smaller values than $D0_{22}$ and N_2M_2 . The interactions $V(8)$'s take a negative value (ordering tendency) in the present simulations for A_3B and A_2B . The interactions suppress the formation of like-atom pairs in the eighth coordinate shells. As a results, the development of $D0_{22}$ and N_2M_2 structures are prevented, while the ordering into $D1_a$ or Pt_2Mo structures can progress. The clustering tendency due to

Fig. 7 Warren-Cowley parameters $\alpha(n)$'s of the relevant ordered structures. Horizontal and vertical denote the n -th coordinate shells and the values of $\alpha(n)$'s, respectively.

positive $V(5)$'s plays a similar role in the course of $D1_a$ ordering at A_4B composition⁽¹⁵⁾.

IV. Conclusion

In the present study, the ordering mechanisms in fcc-based Ni-Mo alloys have been investigated by Monte Carlo simulations. When the pairwise atomic interactions up to the eighth coordinate shells are taken into account, the simulation results are consistent with changes of electron diffraction pattern during the ordering processes in Ni_4Mo , Ni_3Mo and Ni_2Mo . Short range ordering in the early stage generates a mixed state of subunit cell clusters of $D1_a$, $D0_{22}$ and Pt_2Mo structures. The transition from SRO to LRO is attributed to continuous growth of $D1_a$ and/or Pt_2Mo -domains which correspond to the ground state in the system.

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