

ORDER STRUCTURE IN THE EARLY STAGE OF PHASE SEPARATION IN AL-LI ALLOYS - A MONTE CARLO STUDY

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ABSTRACT

Early stage of phase decomposition in dilute Al-Li binary alloys has been investigated by means of Kinetic Ising model up to the second nearest neighbor. The kinetics of phase decomposition accompanying ordering were examined from a viewpoint of cluster image. The kinetics of phase decomposition in the metastable region is characterized by a clearly separated SRO process and clustering process with ordering. Present simulation suggests that in the very early stage of clustering, small clusters are well ordered in short range but not necessarily in long range. Further examination is required to conclude this point.

keywords : *Al-Li alloys, delta prime, ordering, Monte Carlo Method, kinetic Ising model*

1. INTRODUCTION

The kinetics of phase decomposition in Al-Li binary alloys have been intensively investigated both experimentally and theoretically in the last decade. Since it is rather difficult to observe the very early stage of phase decomposition by an experiment, especially by imaging techniques, computer simulation has been used to examine how the ordering behavior relates to the compositional fluctuation. There are two approaches on the computer simulation of phase decomposition in Al-Li alloys. One is a deterministic approach where the kinetics of phase transition are obtained by solving partial differential equation, and the other is a Monte Carlo method. The former one is examined by Chen et al.[1] and Oono et al.[2], and has advantage that the change in the free energy is known explicitly and the microstructural evolution in rather large volume can be simulated. On the other hand, Monte Carlo simulations have advantage in that the atomic arrangement in the real space is readily examined. In the present work, we take this advantage to inquire into the phase decomposition process of dilute Al-Li alloys and compare them with our previous results on concentrated alloys[3].

2. METHODS

The simulation method used in the present simulation is an Ising model with Kawasaki dynamics[4] on a fcc lattice of a size up to 30 unit cells each side. The interaction parameters used in the present simulations, J_1 and J_2 , appearing in the Hamiltonian ;

$$H = \sum_{nn} J_1 \sigma_i \sigma_j + \sum_{2nn} J_2 \sigma_i \sigma_j \quad (1)$$

are -210k and 105k, respectively, according to the cluster variational study by Garland and Sanchez [5]. The transition probability at a given atomic exchange is calculated from the change in H caused by the exchange[6]. The composition and temperature used in the present simulation are shown in

the phase diagram calculated by Garland and Sanchez as Fig. 1. Main feature of the decomposition kinetics are examined at the concentrations of 0.03 and 0.04, which are well below the percolation threshold. For comparison, much more concentrated alloy composition of 0.12 has been examined at the temperatures well above and below the ordering instability.

In the present simulation, we focus our attention on the characteristics of phase separation with ordering in typical metastable regions, i.e., in dilute alloys. The microstructural evolution was examined both from reciprocal and real space. From the Fourier transform of the atomic configuration at each time (Monte Carlo Step, MCS), the structure functions around $k=0$, corresponding small-angle scattering, and that around 100, corresponding to order spot, have been calculated. In order to have a clear image in the analysis in the real space, we define a criterion of a 'cluster' in the following way. First we define a simple cubic lattice whose each lattice point corresponds to four lattice points in the unit cell of original fcc lattice. Each point of the simple cubic lattice has the number of solute atom in the original unit cell as its value. Then a cluster is defined as a unit which is connected by a nearest neighbor bonding on the simple cubic lattice, instead of thinking the connection on the original fcc lattice. Since we are interested in spacial configuration on the concentration, and not in the configuration concerning sublattices when considering clusters, this simplification make the automatic definition of the region 'inside a cluster' much easier. This procedure is described in [3]. After a region 'inside a cluster' is determined, the structure inside a cluster, i.e., concentration, order parameters, etc., and their evolution are calculated.

3. RESULTS AND DISCUSSION

3.1 Scattering intensity

Change in the peak intensities of SAS and 100 obtained for 3%Li and 4at% Li at $T=1.0$ are shown in Fig.2. For 3%Li, the change in the peak intensities for SAS and 100 agrees very well. They first show very small change in the early stage, and then after about 100 MCS, start to increase at an temporal power of about 1. As seen in Fig.2b, SAS and 100 for 4at%Li also show two-step increase, namely, first slow increase and second rapid increase after about 60MCS. A closer examination on the 100 peak intensity in the early stage reveals that the 100 intensity for 4%Li increases gradually, while no clear increase is observed for 3%Li. Since SAS intensity represents the spatial change in the concentration and 100 represents that of order parameter, the second stage of phase separation where the temporal evolution of SAS and 100 peak intensity agrees suggests that a well ordered cluster image, i.e., formation of δ' precipitate is formed in

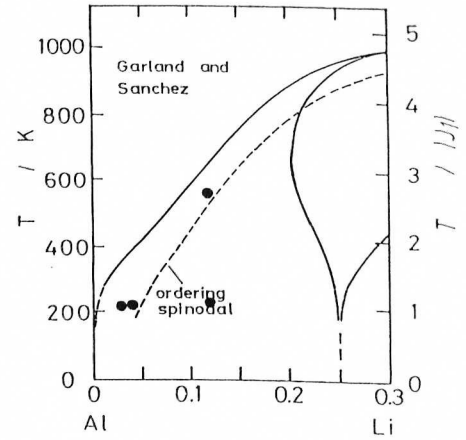


Fig.1 Phase diagram of Al-Li system on Ising lattice [3]

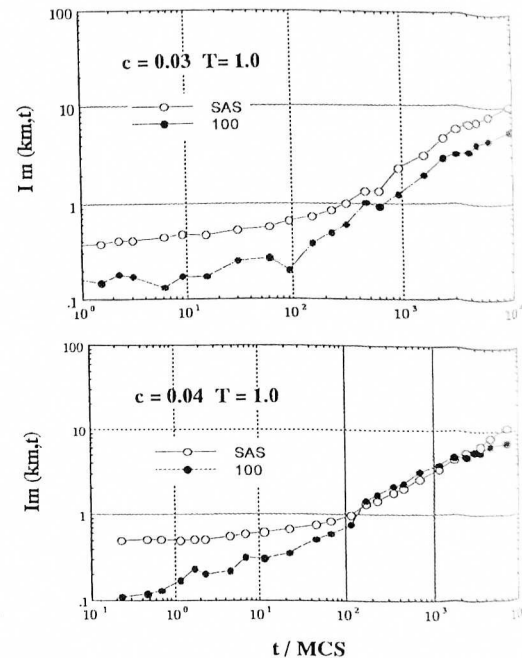


Fig.2 Evolution of the peak intensity for SAS and 100 for 3%Li (a) and 4%Li (b)

this stage.

This suggestion leads to a question whether the increase in the 100 intensity as observed in the early stage for 4% is essential precursory structural change or not.

In order to obtain better insight into the origin of the two step increase as shown above, the evolution of peak intensity at higher concentration in metastable region (well above the ordering instability) and in unstable region (well below the ordering instability) were examined. Figure 3 shows the change in the peak intensities for 12%Li at $T=2.6J_1$, i.e., 546K. As shown in Fig.1, this condition lies well inside the metastable region, and from the classification of the region given by Khachaturyan et al [7], corresponds to 'nucleation of δ' precipitates, 'region D'. It is seen that the peak intensities for SAS and 100 remain almost constant in the intermediate time range, i.e., from about 10 to 100 MC, and then increase at the same temporal power law in the late stage. The most significant difference in the kinetics between the dilute and concentrated alloys in the metastable region appears in the very early stage. The change in the 100 intensity for 3%Li gives no clear increase in the very early stage, i.e., less than several MCS. In contrast, figure 3 shows a rapid increase in the 100 intensity within a couple of MCS. This increase should be explained in terms of short-range ordering, since the time scale is reasonable for the process, and also the ordering does not develop any more after several MCS.

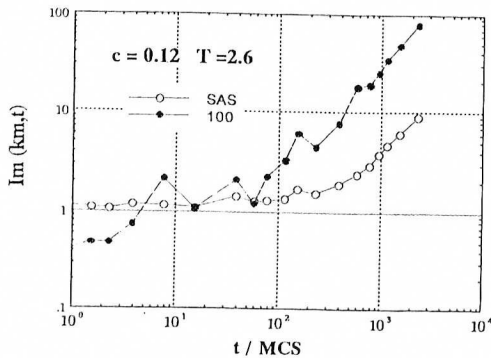


Fig. 3 Peak intensity for 12%Li above the ordering instability

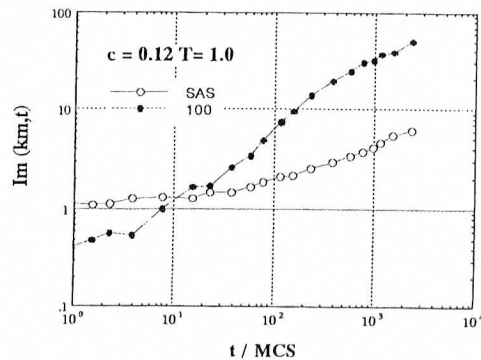


Fig. 4 Peak intensity for 12%Li below the ordering instability

Figure 4 shows the change in the peak intensities for the same composition but at lower temperature, i.e., at $T=1.0J_1$. From Fig. 1, the system is unstable with respect to ordering. The temporal behavior of the peak intensities also agrees in the late stage, i.e., after 500MCS in this condition. Comparing the change of 100 intensity in the first several MCS with that of Fig.3, the increase in the 100 intensity at $T=1.0J_1$ is also similar to that at $T=2.6J_1$. However, remarkable difference appears in the next stage. At $T=1.0J_1$, the intensity continues to increase monotonically up to the late stage where the temporal power law for SAS and 100 agrees. This result suggests that under the ordering instability, a smooth takeover from short-range ordering to long range ordering occurs, while the development of short-range ordering slowed down to reach an apparent incubation in the metastable region, even under the condition that the composition is well above the percolation threshold.

Therefore, it is worthwhile examining the structural evolution of dilute alloys in detail, in order to understand the kinetics of phase decomposition with ordering in the metastable regions. Use of

dilute composition has advantage that the real-space analysis is free from the complication stemming from percolation, which is important in concentrated alloys. In the next section, the structural change inside the clusters during phase decomposition is analyzed for dilute alloys.

3.2 Real-space analysis of clusters

In a discrete lattice model, it is necessary to define the 'boundary' to separate inside and outside a cluster. The definition used in the present analysis is mentioned in brief above and also in [1]. In inhomogeneous systems, it is important to distinguish the average structure and the local structure, e.g., the structure inside the cluster. Therefore, we first calculate the cluster distribution and then the structures inside these clusters. Figure 5 shows the evolution of the cluster size distribution for 3%Li during aging at $1.0J_1$. The cluster size is given by the number of simple lattice sites in a cluster as defined in the previous section. In the very early stage of several MCS, the cluster size distribution decreases monotonically as the size increases. Then at 15.4MCS, the population of larger cluster increases at the cost of smaller clusters, namely, monomer or dimers. The population of these small clusters decreases up to 2000 MCS, where the distribution of small cluster represents a cluster distribution in the matrix at $T=1.0J_1$. The population of larger cluster continues to grow throughout the process, giving increase in the position of the shoulder in size distribution and decrease in the height of the shoulder. This evolution of size distribution qualitatively agrees with that of simple phase separation systems, as reported by Binder et al[8]. Comparing Fig. 2a and 5, it is seen that a continuous growth of clusters is observed even before apparent increase in the peak intensities in Fig.2a is observed.

Before examining the structure inside clusters, it is worthwhile checking the effect of surface on the structure parameters inside clusters. Figure 6 shows the size effect on the coordination number for simple cubic lattice, corresponding to the next nearest neighbor bonding of L12 structure. For example, if the coordination number of next nearest neighbor bonding inside a cluster of a size of 16 is calculated to be 3.4, it means that the order structure inside the cluster is nearly perfect, whereas the order structure has either two dimensional nature or the cluster contains some antiphase structures if the size is 64.

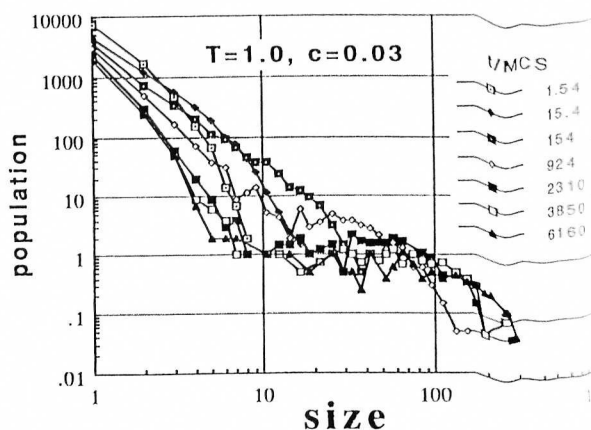


Fig.5 Size distribution for 3%Li

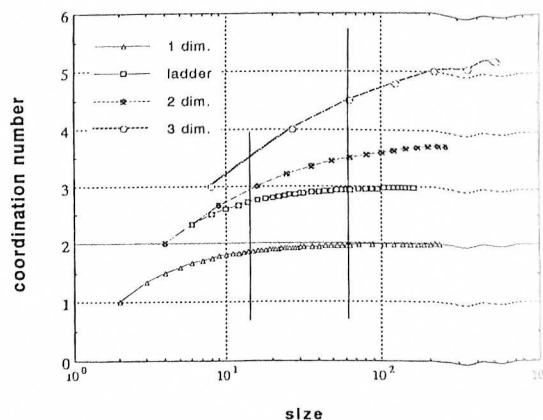


Fig. 6 Size effect on the coordination number

The change in the coordination number of second nearest Li-Li bonds inside clusters for several classes of size are shown in Fig. 7. In the early stage before 300 MCS, it is seen that the average coordination number inside clusters are almost the same except the smallest ones. It means that the deviation from a perfect order does not come from the surface of precipitates, but the imperfect order structure inside clusters in this stage. In the later stage, the coordination number for the smallest ones comes very close to 0, meaning that the most of small clusters left in the matrix are monomers. On the other hand, the coordination number for larger clusters increases monotonically, and exceeds 4.0 at 4000MCS.

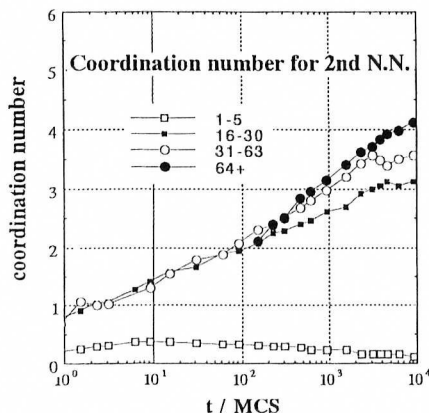


Fig.7 Second nearest coordination number for Li.

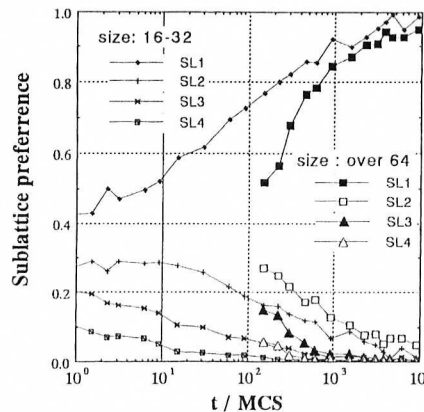


Fig.8 Sublattice preference of Li in clusters

There are two possibilities to account for the lower Li-Li coordination number for the next nearest neighbor inside clusters. One is that the order structure in the cluster has lower dimensional nature. For example, if the next nearest neighbor of Li-Li coordination has rather two dimensional nature, the maximum coordination number is 4. Another possibility is that the cluster contains antiphase domains, which decrease the effective domain size. Since the SRO for the nearest neighbor inside the clusters converges to $-1/3$ within about 10 MCS, decrease of coordination number due to antisite Li is not possible. In order to examine the existence of antiphase domains inside a cluster, temporal evolution of the sublattice preference inside clusters are shown in Fig. 8. The sublattice preference is defined in the following way. When a cluster is defined, one can define a sublattice for the cluster. Then all the Li atoms are counted up to see on which of the four sublattice the atoms are. Then the most dominant sublattice are named sublattice 1 (SL1) and then the second as SL2, etc. Since each clusters are separate each other, SL1 for a cluster does not necessarily the same sublattice of SL1 for another. The values given in Fig.8 are the averages over the range of cluster size given in the figure. It is clearly seen that before short range ordering in the nearest neighbor completed, i.e., earlier than 10-20 MCS, the structure of the cluster is far from a single domain. At 1.0 MCS, clusters with the size between 16 and 32 have all the possible domains with considerably large probability in them. As the clustering proceeds, the most dominant sublattice grows very rapidly, and at the time where SAS intensity is visible, i.e, about 300MCS, only the most dominant and the second dominant sublattice can survive. The preference increases as the aging time increases, and eventually more than 90% solute atoms are on the same sublattice after 2000 MCS. Therefore, a lower coordination number observed in Fig. 7 should be due to the existence of antiphase domains, which makes the effective domain size smaller.

Figure 8 suggests that the structure of clusters formed in the initial stage is well ordered in the short range, but not enough in the long range. In order to answer the question whether this is really the case for the early stage of phase decomposition in real dilute Al-Li alloys, we need further investigation on the following points.

- 1) The effect of vacancy on the kinetics.
- 2) Effect of the range of interaction potential.

The second question is not very important in the present work, since the contribution of longer range interaction is negligibly small under the process of large supersaturation. However, the first question is an important one. This point affects the present results in two ways. One is that the introduction of vacancy might change the effective atomic transport required for clustering. The second one is that vacancy might change the stability of partially ordered structure, or in other words, the stability of order/disorder interface and antiphase boundary. When a vacancy is introduced in the lattice, the change in the energy on exchange is not described in terms of the interaction parameter, $\omega = (E_{AA} + E_{BB})/2 - E_{AB}$ any more [9,10]. The parameter is divided into two parameters, $(E_{AA} - E_{AB})$ and $(E_{BB} - E_{AB})$, and an additional parameter giving vacancy-solute binding energy. The first point is less critical in the present situation, where separated clusters are formed in the matrix, where rapid depletion of solute atoms occurs due to low solubility at low temperatures. However, the second one is not negligible since the metastability of SRO state against LRO should strongly depend on the asymmetry of the energy difference described above. At this moment, a reasonable estimate of this stability is still under way.

4. CONCLUSION

A Monte Carlo simulation with interactions up to the second nearest neighbor was applied to the phase decomposition of dilute Al-Li alloys. It is concluded that ;

1. The structure change in the metastable region is characterized by a well separated SRO and LRO processes.
2. The order structure in small clusters formed in the early stage are not completely ordered at very low temperatures. However, the stability of these transient structure needs further examination.
3. As the clusters grow to several unit cells a side, they tend to become single domain.

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