ISSN 1063-7834, Physics of the Solid State, 2014, Vol. 56, No. 4, pp. 780–784. © Pleiades Publishing, Ltd., 2014.
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PHASE TRANSITIONS

Anomalous Dispersed States of Alloys Caused by Segregation of Impurities at Phase Interfaces

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Received October 2, 2013

Abstract—The diffusion in alloys with tendency to impurity segregation at phase interfaces has been simulated by the Monte Carlo method. It has been shown that at the segregation energy higher than the critical value, dispersity of the system increases due to the suppression of coagulation of phase particles. The effect mathematically represents the violation of the Lifshitz–Slyozov kinetics of an infinite growth of phase particles, which is similar to the anomalous kinetics of grain growth in systems with an impurity. The existence of the equilibrium grain size due to the equilibrium grain size caused by the impurity segregation at grain boundaries was previously predicted by Weissmuller and is now confirmed experimentally. Thus, this study generalizes the Weissmuller effect to the thermodynamics of the decomposition in alloys.

DOI: 10.1134/S1063783414040283

1. INTRODUCTION

In contrast to the surface and grain-boundary segregations, which are studied well experimentally and theoretically [1–5], segregations at phase interfaces, which appear in multicomponent alloys, are poorly understood. However, they exist and can also be of practical importance, determining the operational characteristics of the material (strength, plasticity, creep, electrical and magnetic properties). For example, in recent study [6], when studying the Al–Cu–Ag dispersed alloy, which is used in aerospace industry, Ag segregations of two atomic layers wide were found on dislocations bordering the boundary of Al_2Cu precipitates in the Al matrix. The authors of [7] studied segregations of Au at the interface of the Cu-depleted and Cu-enriched phases in the Ag–Cu–Au alloy. The authors of [8] studied segregations of Cu at the "metal–oxide" phase interface during corrosion of Ni. Segregations of sulfur at the Al–Al_2O_3 phase interface [9], carbon at the NiAl–Al_2O_3 interface, and chromium at the FeCrAl–Al_2O_3 interface [10] are also known. One of the first theoretical investigations of segregations at phase interfaces was performed in [11], where the regular solid solution model was used to describe segregations of Au at the interface between the copper-depleted and copper-enriched phases in the Ag–Cu–Au ternary system. The authors of [12] investigated the same system by the Monte Carlo method, and the authors of [13] performed similar simulation for segregations of Cu at the interface between the Ni-depleted and Ni-enriched phases in the Ni–Ag–Cu ternary alloy.

Segregations at the phase interface should be distinguished from the interlayer of the equilibrium third phase. The main criterion of the distinction is the fact that the interlayer of the equilibrium phase infinitely broadens with time, while the width of the segregation layer during the coagulation of precipitates reaches the equilibrium value (of the order of the width of the phase interface) and further remains unchanged. Precipitation of equilibrium phases is controlled by bulk values of mixing energies of components, while the formation of the segregation layer is caused by the local variation of alloy properties on the phase interface. The latter means that the theory developed for segregations at grain boundaries, including isotherms by McLean [3] and Fowler and Guggenheim [14], kinetic equations [4], and the features of segregations in nanosize samples [5], is applicable for the description of segregations at phase interfaces.

An interesting prediction of the theory of grain-boundary segregations is the anomalous kinetics of the grain growth due to decreasing the system energy during the impurity segregation at grain boundaries [15]. In contrast with pure metal, where the growth of large grains at the expense of small ones is infinite in time and caused by the tendency of the system to decrease the total energy of grain boundaries, the energy of the grain boundary in the system with the impurity can turn to zero due to the impurity segregation leading to the appearance of the equilibrium grain size. This effect is confirmed experimentally [16–18] and by the results of numerical simulation [19]. However, the possibility of the synthesis of equilibrium dispersed microstructures (in the course of the spinodal decomposition or during annealing of the two-phase state) due to the impurity segregation at the phase boundary, which follows from the abovementioned analogy, was not apparently discussed previously. This study fills in this gap.

2. FORMULATION OF THE MODEL. KAWASAKI–MONTE-CARLO ALGORITHM

The feature of this problem is turning to zero of the surface energy of a phase particle during the impurity segregation at the phase interface. In this case, the Cahn–Hilliard differential equations [20] are not applicable since the solution discontinuous by coordinates appears. A similar situation occurs when studying the lamellar microstructures in liquid mixtures, where the continual equations [21, 22] with the Ginzburg–Landau functional of the form $G\{\eta\} = \int[g(\eta) + \kappa R^2(\nabla\eta)^2 + \mathcal{N}(\Delta\eta)^2]d\mathbf{r}$ are used, where $g(\eta)$ is the local density of the internal energy; η is the order parameter; $\kappa R^2(\nabla\eta)^2$ is the contribution to energy associated with the phase interface (R is the width of the phase interface and κ is the energy coefficient); and $\mathcal{N}(\Delta\eta)^2$ is the auxiliary contribution, which ensures the solution continuity with the selection of $\kappa < 0$. Diffusion equations derived using the functional of this form would contain derivatives with respect to the concentration to the sixth order inclusively. However, in physically simple models with the absence of lattice dynamics, the transition to continual equations with high-order derivatives is unjustified. The Monte Carlo (MC) simulation by the Kawasaki algorithm [23] gives a more exact solution, which is simpler in the technical implementation. In this case, the contribution of the form $\mathcal{N}(\Delta\eta)^2$, which is present in the functional, is not required since the problem of the solution continuity does not appear in the MC simulation.

For clearness of representation of results, let us consider the 2D model with a simple square lattice. To compensate a decrease in the coordination number when going to 2D model, we assume that the interaction radius of the atoms includes three coordination spheres (CS), so that each atom interacts with 12 neighbors ($Z = 12$). In this study, we limit ourselves by the consideration of binary and ternary alloys. The Hamiltonian of the system has the form

$$H = E_0 + \sum_{\{i,j\}}\left[\sum_{\alpha}(\varepsilon_\alpha + \sigma_\alpha^{(i,j)})n_\alpha^{(i,j)} + \frac{1}{2}\sum_{\alpha\beta,\,kl}\nu_{\alpha\beta}^{(i,j;\,k,\,l)}n_\alpha^{(i,j)}n_\beta^{(k,\,l)}\right], \quad (1)$$

where indices α and β denote the types of impurity atoms, $\alpha = \{A, B\}$, $\beta = \{A, B\}$, (i, j) and (k, l) are the lattice sites, $n_\alpha^{(i,j)}$ is the occupation number equal to 1 if the atom of type α is arranged in site (i, j) and equal to 0 otherwise, ε_α is the dissolution energy of the atom of type α in the matrix, $\nu_{\alpha\beta}^{(i,j;\,k,\,l)}$ is the interaction energy of the atoms of types α and β at a distance determined by sites (i, j) and (k, l), and $\sigma_\alpha^{(i,j)}$ is the interaction energy of the atom of type α with the phase interface (i.e., the segregation energy).

Let us determine the concentration of atoms of type α in site (i, j) by averaging the occupation numbers by 3 CS, $c_\alpha^{(i,j)} = \sum_{\{4CS\}} n_\alpha^{(i,j)}/13$ and, correspondingly, the contribution to energy of the atom of type β at the phase interface equals $\sigma_\beta^{(i,j)} = \tilde{\kappa}_\beta^{(i,j)}[(c_\alpha^{(i+1,j)} - c_\alpha^{(i-1,j)})^2 + (c_\alpha^{(i,j+1)} - c_\alpha^{(i,j-1)})^2]/4$, where $\tilde{\kappa}_\beta^{(i,j)} = \kappa_\beta^{(i,j)} R^2/a^2$, a is the lattice parameter. According to our hypothesis, $\kappa_\beta < 0$, i.e., the energy of atoms of type β lowers with their arrangement at the phase interface.

The Kawasaki MC algorithm consists in the following. A pair of neighboring atoms is selected randomly and energies of the starting configuration E_1 and after rearrangement of atoms in sites E_2 are calculated. A new configuration is accepted unambiguously if $E_2 < E_1$, otherwise it is accepted with probability $P = \exp[(E_1 - E_2)/(kT)]$. Then another pair of nearest neighbors is selected, and the algorithm is repeated. We note that it follows from here that the solution is independent of volume values of dissolution energies ε_α since the corresponding contribution to (1) remains unchanged with the atomic rearrangement.

Calculations were performed for a 250 × 250 network, the boundary conditions were taken periodic, and diffusivities for all types of atoms were accepted identical. Further, for simplicity, we will accept atoms of types A, B, and C, as well as the phases corresponding to them by the same letters.

3. RESULTS OF SIMULATION

Let us initially consider a binary alloy in which the decomposition occurs below the critical temperature by virtue of $\nu < 0$, and the energy of atoms of type B decreases at the AB phase interface. Such situation can apparently appear with the violation of lattice coherency at the phase interface so that the phase particle in essence is a new grain and the phase interface simultaneously serves as a grain boundary. Segregations at the phase interface cannot be found experimentally in this alloy since their chemical composition approximately coincides with the composition of one of the phases. However, it is shown below that the presence of the additional contribution in the region of the phase interface in (1) leads to the dramatic variation in morphology of phase particles and the equilibrium state of the alloy.

Figure 1 shows characteristic morphologies of precipitates in alloys with various compositions obtained after the prolonged exposure at the start from the

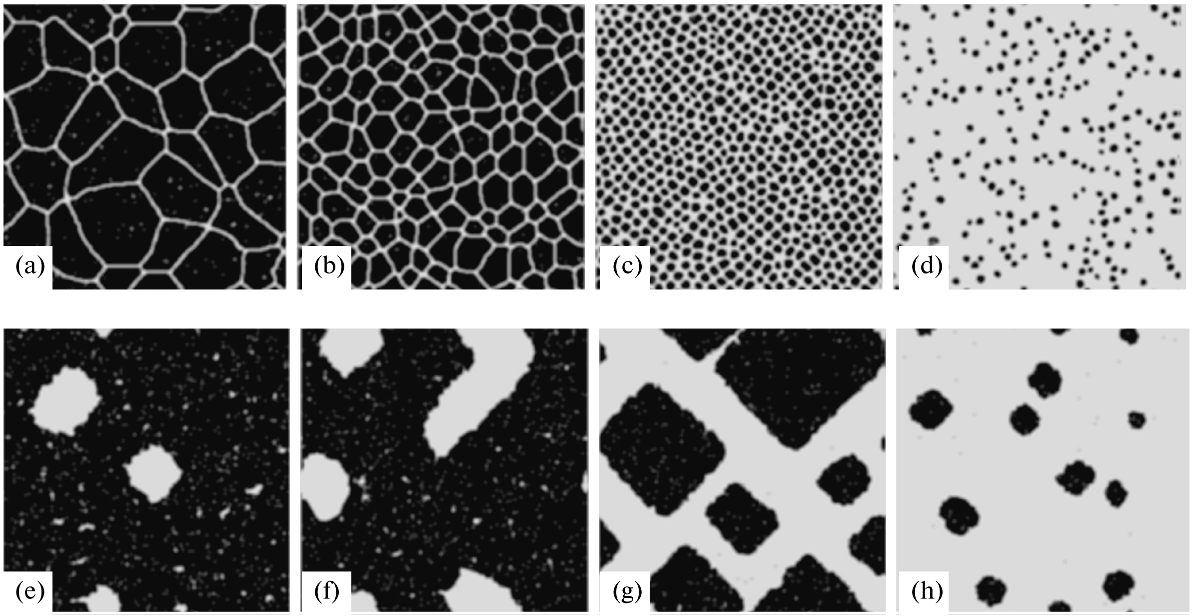

Fig. 1. Distribution of components in a binary alloy at the start from the homogeneous state and prolonged exposure times ($\sim 1E+09$ rearrangements of dissimilar atoms); $Z\nu/kT = -11$; $\tilde{\kappa}_B(Z\nu)$ = (a–d) 16 and (e–h) 4; $\langle C_A \rangle$ = (a, e) 0.1, (b, f) 0.20, (c, g) 0.50, and (d, h) 0.10.

homogeneous initial state. The concentration of component A is denoted in patterns by gradations of gray color (white color corresponds to the value of concentration of 1 and black color—to 0). We can see from comparison of fragments in Figs. 1a–1d and Figs. 1e–1h that if ratio $\tilde{\kappa}_B/(Z\nu)$ is higher than the critical one (the upper row of patterns), the dispersed structure of phase particles is formed. The morphology of this microstructure substantially depends on the alloy composition. If atoms of type A are the impurity (i.e., the minority atoms), a cellular microstructure appears, which is similar qualitatively to a grain structure, with segregations of atoms of type A on the grain boundaries (Fig. 1a). In this case, the average cell size decreases as concentration $\langle C_A \rangle$ average over the sample increases (Figs. 1a, 1b). If the impurity is represented by atoms B, then these atoms combine into clusters, which have no stimulus for the further growth. The density of the number of clusters in the volume unit rises as $\langle C_B \rangle$ increases in this case (Figs. 1c, 1d). The short-range order can be followed in the arrangement of clusters. Finally, if $\tilde{\kappa}/(Z\nu)$ is lower than the critical value, other parameters being unchanged, the morphologies of precipitates typical of the spinodal decomposition are observed (Figs. 1e–1h).

It should be noted that all structures presented in Figs. 1a–1d are close to equilibrium and independent of the selection of the initial state. In this case, the dispersity of the system can increase during its evolution. To illustrate this fact, Fig. 2 represents the patterns of the transformation kinetics at the start from a two-phase state. We can see that a cellular structure similar to that one presented in Fig. 1b is formed at a considerable exposure. At low values of $\langle C_A \rangle$, this transformation kinetics is similar to an anomalous kinetics of the grain growth with the segregation of impurity atoms at intergrain boundaries (the Weissmuller effect [15]). However, it is noteworthy that in this calculation, in contrast to [15], an anomalous kinetics appears as a result of the joint effect of two factors—thermodynamic instability of the alloy ($\nu < 0$) and lowering the energy of matrix atoms (type B) in the concentration gradient region rather than as a result of lowering the energy of impurity atoms (type A) at the phase interface.

Let us now consider the formation of dispersed structures in the ternary alloy. We accept for simplicity that $\nu_{AA} < 0$, other $\nu_{\alpha\beta} = 0$; $\sigma_A = 0$, $\sigma_B = \kappa_B R^2(\nabla c_A)^2$. Thus, the decomposition due to the attraction of atoms of type A occurs below the critical temperature in the system under consideration, while atoms of type B interact with the boundaries of appearing phase particles.

Figure 3 shows the distribution patterns of concentrations in various instants at the start from a nonequilibrium two-phase state A–C with the impurity of component B distributed homogeneously in both phases. The selection of such starting state makes it possible to observe the effect of various transformation mechanisms during one computation.

Clusters of atoms of type B are formed in the phase formed by component A for short times by the mechanism of spinodal decomposition (i.e., under the effect of factor $\nu_{AA} < 0$). However, the further transformation kinetics substantially differs from the coagulation of precipitates, which is characteristic for the spinodal

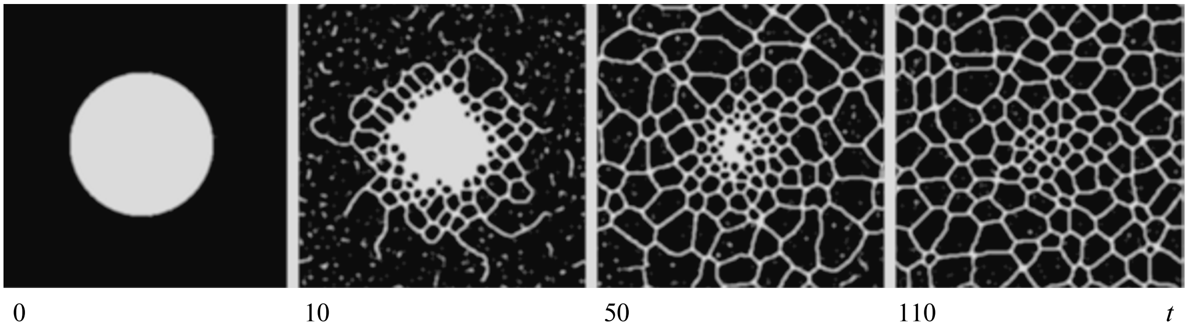

Fig. 2. Evolution of a binary alloy to the equilibrium state at $\tilde{\kappa}_B/(Z\nu) = 16$, $\langle C_A \rangle = 0.2$, and $Z\nu/(kT) = -11$. Time unit t corresponds to $1E + 07$ rearrangements of dissimilar atoms.

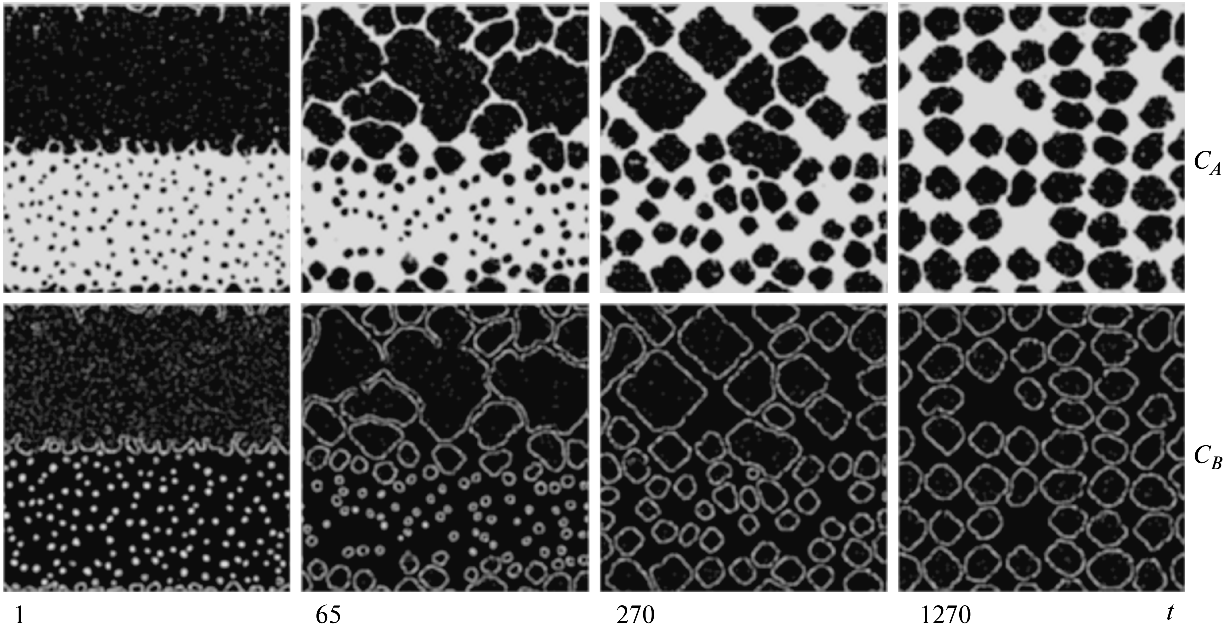

Fig. 3. Evolution of a ternary alloy to the equilibrium state at $\tilde{\kappa}_B/(Z\nu_{AA}) = 16$, $\langle C_B \rangle = 0.1$, and $Z\nu_{AA}/(kT) = -11$; other $\nu_{\alpha\beta} = 0$. Time unit t corresponds to $1E + 07$ rearrangements of dissimilar atoms.

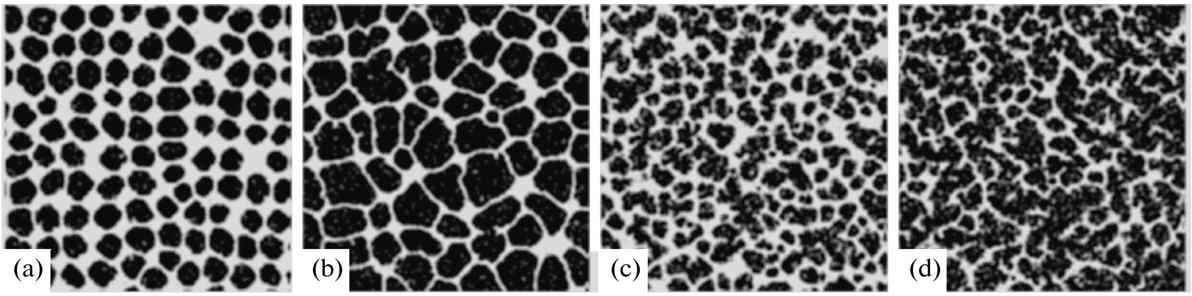

Fig. 4. Concentration distributions of component A attained at prolonged exposure times ($\sim 1E + 10$ rearrangements of dissimilar atoms); $\langle C_B \rangle = 0.15$; $\tilde{\kappa}_B/(Z\nu_{AA}) = 16$; $Z\nu_{AA}/(kT) =$ (a, b) -11 and (c, d) -9; $\langle C_A \rangle =$ (a, c) 0.42 and (b, d) 0.30.

decomposition. Phase particles of component B appeared in phase A are saturated with atoms of type C so that component B is forced out on the phase interfaces. In parallel with this process, steaks of type A atoms decorated by segregations of type B atoms are formed in phase C. The growth process of precipitates in phase A and subdivision of phase C finally lead to the formation of a dispersed microstructure with the short-range order of phase particles. It is seen from Fig. 3 that even superdefects of the vacancy type can occur in this microstructure. This microstructure qualitatively differs from the cluster structure in a binary alloy (Figs. 1c, 1d) since the size of phase particles is determined by the impurity concentration $\langle C_B\rangle$ and can be much higher than the cluster size.

Figure 4 represents the concentration distributions attained at prolonged exposure times in a system with the concentration of impurity atoms $\langle C_B\rangle$ increased by a factor of 1.5 at different concentrations $\langle C_A\rangle$ and temperature. It is seen that the microstructure dispersity increases as $\langle C_B\rangle$ increases (compare Fig. 4a and Fig. 3). To the contrary, as $\langle C_A\rangle$ lowers, precipitates are coarsened, their shape becomes less rounded, and the pattern approaches qualitatively the case of the binary alloy (compare Fig. 4b and Figs. 1a, 1b). As the temperature elevates, precipitates become finer and loss the regular form (Figs. 4c, 4d); however, a developed short-range order in the atomic arrangement occurs for a certain temperature range.

4. CONCLUSIONS

Modulated structures and dispersed states are often observed in alloys and are conventionally associated with the role of elastic stresses [24, 25], which are maximal at the coherent matching the lattices of appearing phases. In this study, we assume a possible additional mechanism of appearance of dispersed structures in certain systems, which is associated with lowering (to a critical value) of the dissolution energy for one-type atoms at the phase interface. This mechanism should be most clearly pronounced in conditions of incoherent lattice matching. It is shown that this mechanism can lead to the formation of dispersed equilibrium structures both in binary and ternary alloys. Either cellular or cluster structures with the short-range order of phase particles are formed in binary alloys depending on the composition. The cellular structures are formally equivalent to the equilibrium grain structure appearing with the impurity segregation at grain boundaries (the Weissmuller effect [15]). Superstructures with the short-range order of phase particles are also formed in ternary alloys due to the segregation of the third component at the phase interface, and the phase particles size increases as the concentration of the third component lowers. Microstructures with the irregular shape of phase particles but with the developed short-range order in the atomic arrangement are observed as the temperature is elevated.

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Translated by N. Korovin