Kinetics of Phase Separation in Fe–Cr–Mo Ternary Alloys

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Numerical simulations were performed using a model based on the Cahn-Hilliard equation in order to investigate asymptotic behavior of a minor element associated with phase decomposition of the major element in Fe–Cr–Mo ternary alloys. Bifurcation of peaks of Mo along peak tops of Cr concentration occurs in an Fe–40 at%Cr–5 at%Mo alloy at 800 K. Bifurcation of peaks of Cr is also shown in an Fe–40 at%Mo–5 at%Cr alloy at 800 K. The amplitude of a peak of Mo in an Fe–40 at%Cr–5 at%Mo alloy at 1023 K increases with time. The asymptotic tops of Cr concentration occurs in an Fe–40 at%Cr–5 at%Mo alloy at 800 K. Bifurcation of peaks of Cr is also shown in an Fe–40 at%Mo–5 at%Cr alloy at 800 K. The knowledge of microstructural evolutions associated with phase separation is important for materials design of Fe-based alloys.

Behavior of phase separation in ternary alloys2,3) is known to be different from that of binary alloys. A numerical simulation of phase separation in Fe–Cr–Mo ternary alloys has been reported by Honjo and Saito.3) They reported that a periodic microstructure including high Cr and Mo was formed by phase separation in an Fe–40 at%Cr–3 at%Mo alloy and that the Mo rich regions were formed inside the Cr rich region. Furthermore there was a little decrease in the amplitude of Mo concentration at the peak positions of Cr. However, the mechanisms of forming the bifurcation of peaks of Mo is not clear.

This paper deals with kinetics of phase separation in ternary alloys, especially asymptotic behavior of a minor element such as Mo in the above alloy associated with the decomposition of the major element. Numerical simulation models based on the Cahn-Hilliard equation4,5) have been applied to the investigation of phase separation in Fe–Cr–Mo ternary alloys. Simulated asymptotic behavior of Mo or Cr associated with decomposition of Cr or Mo is compared with that predicted by the theory proposed by the present authors.6)

1. Introduction

Atomic scale microstructures resulting from heat treatment sometimes deteriorate properties of Fe-based alloys. For example, the ferrite phase in duplex stainless steels is thermomechanically unstable at service temperatures and hardens and embrittles due to the formation of modulated structure via phase separation.7) The knowledge of microstructural evolutions associated with phase separation is important for materials design of Fe-based alloys.

Behavior of phase separation in ternary alloys2,3) is known to be different from that of binary alloys. A numerical simulation of phase separation in Fe–Cr–Mo ternary alloys has been reported by Honjo and Saito.3) They reported that a periodic microstructure including high Cr and Mo was formed by phase separation in an Fe–40 at%Cr–3 at%Mo alloy and that the Mo rich regions were formed inside the Cr rich region. Furthermore there was a little decrease in the amplitude of Mo concentration at the peak positions of Cr. However, the mechanisms of forming the bifurcation of peaks of Mo is not clear.

This paper deals with kinetics of phase separation in ternary alloys, especially asymptotic behavior of a minor element such as Mo in the above alloy associated with the decomposition of the major element. Numerical simulation models based on the Cahn-Hilliard equation4,5) have been applied to the investigation of phase separation in Fe–Cr–Mo ternary alloys. Simulated asymptotic behavior of Mo or Cr associated with decomposition of Cr or Mo is compared with that predicted by the theory proposed by the present authors.6)

2. Model

2.1 The Cahn-Hilliard equation for a ternary alloy

The one-dimensional Cahn-Hilliard equation for an Fe–X–Y ternary alloy is given by

\[
\begin{align*}
\frac{\partial c_X}{\partial t} &= M_X \left[ \frac{\partial^2 f_1}{\partial c_X^2} + \frac{\partial^2 f_1}{\partial c_Y \partial c_Y} \frac{\partial^2 c_X}{\partial x^2} + \frac{\partial^2 f_1}{\partial c_Y^2} \frac{\partial^2 c_X}{\partial x^2} \right] \\
\frac{\partial c_Y}{\partial t} &= M_Y \left[ \frac{\partial^2 f_1}{\partial c_Y^2} + \frac{\partial^2 f_1}{\partial c_X \partial c_Y} \frac{\partial^2 c_Y}{\partial x^2} + \frac{\partial^2 f_1}{\partial c_X^2} \frac{\partial^2 c_Y}{\partial x^2} \right]
\end{align*}
\]

With use of the regular solution model, the local free energy is written as

\[
f_i = f_{Fe}(1 - c_X - c_Y) + f_{Xc}c_X + f_{Yc}c_Y + f_{X,Y}c_Xc_Y + f_{X,Y}c_Xc_Y + RT \ln(1 - c_X - c_Y)
\]

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where \( R \) is the gas constant, \( T \) is the absolute temperature, \( \Omega_{\text{FeX}}, \Omega_{\text{FeY}} \) and \( \Omega_{XY} \) are interaction parameters and \( f_{\text{Fe}}, f_{\text{X}} \) and \( f_{\text{Y}} \) are the molar free energy of pure Fe, pure X and pure Y, respectively. From eq. (5) it follows that

\[
\frac{\partial^2 f_{\text{X}}}{\partial c_X^2} = -2\Omega_{\text{FeX}} + RT \left( \frac{1}{c_X} + \frac{1}{1 - c_X - c_Y} \right)
\]

(6)

\[
\frac{\partial^2 f_{\text{Y}}}{\partial c_Y^2} = -2\Omega_{\text{FeY}} + RT \left( \frac{1}{c_Y} + \frac{1}{1 - c_X - c_Y} \right)
\]

(7)

\[
\frac{\partial^2 f_{\text{X}}}{\partial c_X \partial c_Y} = \Omega_{XY} - \Omega_{\text{FeX}} - \Omega_{\text{FeY}} + RT \frac{1}{1 - c_X - c_Y}
\]

(8)

### 2.2 Conditions of numerical simulations

Numerical simulations based on the Cahn-Hilliard equation were performed for Fe–Cr–Mo ternary alloys. Table 1 shows the conditions used for simulation. The mobilities and the gradient energy coefficients for Fe–Cr–Mo ternary alloys are

\[
M_{\text{Cr}} = \frac{c_1 \cdot D_{\text{Cr}}}{2\Omega_{\text{FeCr}} - 4RT}, \quad M_{\text{Mo}} = \frac{c_1 \cdot D_{\text{Mo}}}{2\Omega_{\text{FeMo}} - 4RT}
\]

(9)

\[
K_{\text{Cr}} = \frac{1}{2} \cdot a_0^2 \cdot \Omega_{\text{FeCr}}, \quad K_{\text{Mo}} = \frac{1}{2} \cdot a_0^2 \cdot \Omega_{\text{FeMo}}
\]

(10)

\[
L_{\text{CrMo}} = L_{\text{MoCr}} = \frac{1}{2} \cdot a_0^2 \left( \Omega_{\text{CrMo}} - \Omega_{\text{FeCr}} - \Omega_{\text{FeMo}} \right)
\]

(11)

where \( a_0 \) is the lattice constant, \( D_{\text{Cr}} \) is the diffusion coefficient of Cr in Fe–50 at%Cr steel and \( D_{\text{Mo}} \) is the diffusion coefficient of Mo in Fe–50 at%Mo steel. The following values for \( D_{\text{Cr}} \) and \( D_{\text{Mo}} \) were used for simulation.

\[
D_{\text{Cr}} = 0.19 \exp\left(-\frac{-246000}{RT}\right)
\]

(12)

\[
D_{\text{Mo}} = 0.29 \exp\left(-\frac{-264000}{RT}\right)
\]

(13)

The constant \( c_1 \) is an adjustable parameter which modifies time scale in order that good agreement between calculated and observed phase separation kinetics is obtained. The constant 0.01 for \( c_1 \) was used in the present simulation. The interaction parameters are

\[
\Omega_{\text{FeCr}} = 18.6 \text{ kJ/mol}, \quad \Omega_{\text{FeMo}} = 18.2 \text{ kJ/mol}, \quad \Omega_{\text{CrMo}} = 8.0 \text{ kJ/mol}
\]

(14)

### 3. Results and Discussion

#### 3.1 Bifurcation of peaks of the minor element associated with decomposition of the major element in Fe-based ternary alloys

Figure 1 shows the variation in the concentration profiles of Cr in an Fe–40 at%Cr–5 at%Mo alloy at 800 K together with that of Mo. The formation of Cr rich regions by phase separation is clearly seen in this figure. A modulated structure of Mo with similar wavelength to that of Cr is observed. However the concentration of Mo at the peak of Cr concentration is found to be decreasing with time. The variation in the concentration profiles of Mo and Cr in an Fe–40 at%Cr–5 at%Cr alloy at 800 K is shown in Fig. 2. The formations of Mo rich regions and a modulated structure of Cr are observed in this figure. The bifurcation of peaks of Cr occurs also in this alloy at the later stage. The behavior of Cr in this alloy is quite similar to that in the Fe–40 at%Cr–5 at%Mo alloy.

The mechanism of bifurcation formation of peaks can be explained by the theory proposed by the present authors. The outline of the theory is as follows. We deal with the case in which the concentration of the X element in an Fe–X–Y ternary alloy, \( c_X \), and the concentration of the Y element, \( c_Y \), satisfy the following conditions

\[
c_X > c_Y, \quad \frac{\partial^2 f_{\text{X}}}{\partial c_X^2} < 0, \quad \frac{\partial^2 f_{\text{Y}}}{\partial c_Y^2} > 0
\]

(15)

A function \( G_Y(t, x, c_X, c_Y, \partial c_X/\partial x, \partial c_Y/\partial x, \partial^2 c_X/\partial x^2, \partial^2 c_Y/\partial x^2, \partial^4 c_X/\partial x^4, \partial^4 c_Y/\partial x^4) \) is defined as

\[
G_Y \left( t, x, c_X, c_Y, \frac{\partial c_X}{\partial x}, \frac{\partial c_Y}{\partial x}, \frac{\partial^2 c_X}{\partial x^2}, \frac{\partial^2 c_Y}{\partial x^2}, \frac{\partial^4 c_X}{\partial x^4}, \frac{\partial^4 c_Y}{\partial x^4} \right)
\]

\[
= M_Y \left\{ \frac{\partial^3 f_{\text{X}}}{\partial c_X \partial c_Y} \frac{\partial^2 c_X}{\partial x^2} + \frac{\partial^3 f_{\text{Y}}}{\partial c_Y \partial c_X} \frac{\partial^2 c_Y}{\partial x^2} + 2 \frac{\partial^3 f_{\text{X}}}{\partial c_X^2} \frac{\partial c_X}{\partial x} \frac{\partial c_Y}{\partial x} \right\}
\]

\[
- L_{XY} \frac{\partial^4 c_X}{\partial x^4} - K_Y \frac{\partial^4 c_Y}{\partial x^4}
\]

(16)

This function satisfies the following condition:

\[
G_Y \left( t, x, c_X, c_Y, 0, \frac{\partial c_Y}{\partial x}, 0, \frac{\partial^2 c_X}{\partial x^2}, \frac{\partial^2 c_Y}{\partial x^2}, \frac{\partial^4 c_X}{\partial x^4}, \frac{\partial^4 c_Y}{\partial x^4} \right)
\]

\[
= M_Y \left\{ \frac{\partial^2 f_{\text{X}}}{\partial c_X^2} \frac{\partial^2 c_X}{\partial x^2} + \frac{\partial^2 f_{\text{Y}}}{\partial c_Y^2} \frac{\partial^2 c_Y}{\partial x^2} + 2 \frac{\partial^3 f_{\text{X}}}{\partial c_X^2} \frac{\partial c_X}{\partial x} \frac{\partial c_Y}{\partial x} \right\}
\]

\[
- L_{XY} \frac{\partial^4 c_X}{\partial x^4} - K_Y \frac{\partial^4 c_Y}{\partial x^4}
\]

(17)

At a peak position \( p(x, t) \)

\[
\frac{\partial c_X}{\partial x} = 0 \quad \frac{\partial^2 c_X}{\partial x^2} < 0.
\]

(18)

Applying the mean value theorem of differential calculus for a compound function, we obtain the following equation for
Fig. 1 Variations of Cr and Mo profiles with time in an Fe–40 at%Cr–5 at%Mo ternary alloy at 800 K.

Fig. 2 Variations of Mo and Cr profiles with time in an Fe–40 at%Mo–5 at%Cr ternary alloy at 800 K.

Equation (19) along a peak top of $c_X$ can be approximated by

$$\frac{\partial c_Y}{\partial t} (x_p, t) \simeq M_Y \frac{\partial^2 f_1}{\partial c_X \partial c_Y} \frac{\partial^2 c_X}{\partial x^2}$$

From eq. (20) it is indicated that the behavior of the Y
elements at a peak position of the X depends on the sign of \( \frac{\partial^2 f_I}{\partial c_X \partial c_Y} \).

If \( \frac{\partial^2 f_I}{\partial c_X \partial c_Y} < 0 \), then we have

\[
\frac{dc_Y(x_p, t)}{dt} > 0
\] (21)

Peaks of \( c_Y \) will be formed at the same position of the peak tops of \( c_X \). The wavelength of the concentration profile of the Y element will be equal to that of the X element. This is the phase separation induced modulated structure. From eq. (8) it follows that

\[
\frac{d}{dt} \left( \frac{\partial^2 f_I}{\partial c_X \partial c_Y} \right) = \frac{RT}{(1 - c_X - c_Y)^2} \left( \frac{dc_X}{dt} + \frac{dc_Y}{dt} \right)
\] (22)

If \( dc_X/dt > 0 \) and \( dc_Y/dt > 0 \) then

\[
\frac{d}{dt} \left( \frac{\partial^2 f_I}{\partial c_X \partial c_Y} \right) > 0
\] (23)

The sign of \( \frac{\partial^2 f_I}{\partial c_X \partial c_Y} \) may change from negative to positive in lower temperatures at which the equilibrium concentration of the X element is high. This indicates that bifurcation of peaks will occur at the later stage of phase decomposition.

The variation in concentration profiles of Cr and Mo in an Fe–40 at%Cr–30 at%Mo alloy at 1025 K is shown in Fig. 3. The concentration of Mo at a peak position of Cr increases with time. The equilibrium concentration of Cr at a high temperature is smaller than that at a lower temperature. In this condition the value of \( RT/(1 - c_{Cr} - c_{Mo}) \) is smaller than the absolute value of \( \Omega_{CrMo} = \Omega_{FeCr} = \Omega_{FeMo} \). So the value of \( \frac{\partial^2 f_I}{\partial c_X \partial c_Y} \) is negative at the later stage. Thus the bifurcation of peaks will not occur in this case.

### 3.2 Phase separation in an Fe–30 at%Cr–30 at%Mo alloy

Next let us consider the case in which both \( c_X \) and \( c_Y \) are within the spinodal region of an Fe–X–Y ternary phase diagram. In this case

\[
c_X \simeq c_Y, \quad \frac{\partial^2 f_I}{\partial c_X^2} < 0, \quad \frac{\partial^2 f_I}{\partial c_Y^2} < 0
\] (24)

It is expected that X and Y elements decompose separately. By repeating the above analyses, we may predict that the amplitude of \( c_Y \) increases at a peak position of the X element and that the amplitude of X element also increases at the peak position of the Y element. The modulated structure of the Y element is expected to be similar to that of the X element. As a result the wavelength of the modulated structure is predicted to be shorter than those of Fe–X and Fe–Y binary alloys.

Figure 4 shows the variation in concentration profiles of Cr and Mo in an Fe–30 at%Cr–30 at%Mo alloy. The concentration profile of Cr is quite similar to that of Mo. The wavelength of the modulated structure is smaller than those of Fe–Cr and Fe–Mo binary alloys.

### 3.3 Concentration dependence of atomic mobilities

In our analyses of asymptotic behavior of a minor element in an Fe–X–Y ternary alloy, the atomic mobilities \( M_X \) and \( M_Y \) are assumed to be not dependent on their position in the space. We neglected the concentration dependence of atomic mobilities. Now let us consider the case that the mobilities \( M_X \) and \( M_Y \) are functions of \( c_X \) and \( c_Y \). In this case the Cahn-
Hilliard equation for an Fe–X–Y ternary alloy is given by
\[
\frac{\partial c_X}{\partial t} = M_X \left[ \frac{\partial^2}{\partial x^2} \left( \frac{\partial f_1}{\partial c_X} - K_X \frac{\partial^2 c_X}{\partial x^2} - L_{XY} \frac{\partial^2 c_Y}{\partial x^2} \right) \right] + \frac{\partial M_X}{\partial x} \left[ \frac{\partial}{\partial x} \left( \frac{\partial f_1}{\partial c_X} - K_X \frac{\partial^2 c_X}{\partial x^2} - L_{XY} \frac{\partial^2 c_Y}{\partial x^2} \right) \right]
\]
\[
\frac{\partial c_Y}{\partial t} = M_Y \left[ \frac{\partial^2}{\partial x^2} \left( \frac{\partial f_1}{\partial c_Y} - L_{XY} \frac{\partial^2 c_X}{\partial x^2} - K_Y \frac{\partial^2 c_Y}{\partial x^2} \right) \right] + \frac{\partial M_Y}{\partial x} \left[ \frac{\partial}{\partial x} \left( \frac{\partial f_1}{\partial c_Y} - L_{XY} \frac{\partial^2 c_X}{\partial x^2} - K_Y \frac{\partial^2 c_Y}{\partial x^2} \right) \right]
\]
(25)

The terms \( \frac{\partial M_X}{\partial x} \) and \( \frac{\partial M_Y}{\partial x} \) are rewritten as
\[
\frac{\partial M_X}{\partial x} = \frac{\partial M_X}{\partial c_X} \xi \frac{\partial c_X}{\partial x} + \frac{\partial M_X}{\partial c_Y} \xi \frac{\partial c_Y}{\partial x}
\]
(27)
\[
\frac{\partial M_Y}{\partial x} = \frac{\partial M_Y}{\partial c_X} \xi \frac{\partial c_X}{\partial x} + \frac{\partial M_Y}{\partial c_Y} \xi \frac{\partial c_Y}{\partial x}
\]
(28)

At a peak position of the X element, the above equations yield
\[
\frac{\partial M_X}{\partial x} = \frac{\partial M_X}{\partial c_X} \xi \frac{\partial c_X}{\partial x}
\]
(29)
\[
\frac{\partial M_Y}{\partial x} = \frac{\partial M_Y}{\partial c_Y} \xi \frac{\partial c_Y}{\partial x}
\]
(30)

At the initial stage of phase separation \( \frac{\partial c_Y}{\partial x} \) is very small. Once a peak or a bottom of Y element is formed the term \( \frac{\partial c_Y}{\partial x} \) becomes zero. It follows that the asymptotic behavior of the Y element at a peak top of the X element can be approximated by eq. (20) also in the case that the mobilities of X and Y elements are concentration dependent.

3.4 Applicability of the present analyses

We have investigated the kinetics of phase separation in Fe–Cr–Mo ternary alloys. Numerical simulations based on the Cahn-Hilliard equation for multicomponent systems demonstrated that the theory\(^6\) on asymptotic behavior of the minor element associated with decomposition of the major element is reasonable. Monte Carlo simulations of phase separation in Fe–Cr–Mo ternary alloys are now in progress. Preliminary results\(^10\) are qualitatively in good agreement with the numerical results based on the Cahn-Hilliard equation.

Experimental verifications of the present analyses are left as future problems.

4. Summary

Numerical simulations of phase separation in Fe–Cr–Mo ternary alloys were performed with use of a model based on the Cahn-Hilliard equation in order to investigate asymptotic behavior of a minor element associated with phase decomposition of the major element. The following results are obtained.

1. Bifurcation of peaks of Mo along the peak tops of Cr concentration occurs in an Fe–40 at%Cr–5 at%Mo alloy at 800 K. Bifurcation of peaks of Cr is also shown in an Fe–40 at%Mo–5 at%Cr alloy at 800 K. In these cases, the sign of the second derivative of the chemical free energy \( f_1 \) with respect to the concentration of Cr, \( c_C \), and the concentration of Mo, \( c_{Mo} \), \( \partial^2 f_1 / \partial c_C \partial c_{Mo} \), changes from negative to positive at the later stage.

2. In an Fe–40 at%Cr–5 at%Mo alloy, peaks of the concentration of Mo form along the peak tops of Cr at 1025 K. Once a peak is formed the amplitude of the concentration in-
creases with time.

(3) The asymptotic behavior of Mo or Cr in an Fe–Cr–Mo ternary alloy along a trajectory of a peak top of Cr or Mo, depends on the sign of $\frac{\partial^2 f_1}{\partial c_{Cr} \partial c_{Mo}}$.

(4) For the case in which both $c_{Cr}$ and $c_{Mo}$ are within the spinodal region of an Fe–Cr–Mo ternary phase diagram, the amplitude of Mo increases at the peak positions of Cr and the amplitude of Cr also increases at the peak positions of Mo. The wavelength of the modulated structure is shorter than those of Fe–Cr and Fe–Mo binary alloys.

(5) Simulated asymptotic behavior of Mo and Cr in Fe–Cr–Mo ternary alloys is in good agreement with that predicted by the theory proposed by the present author.

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