1. Introduction

Duplex stainless steels are extensively used in chemical reactors because of several superior properties, namely, high strength, good weldability and high resistance to stress corrosion cracking. However, the ferrite phase in duplex stainless steels is thermodynamically unstable at service temperatures and hardens and embrittles owing to the formation of nanoscale modulated structures via phase separation. Thermal aging embrittlement of duplex stainless steels associated with phase separation in the ferrite phase is known as “475°C embrittlement”. As decomposition occurs, a highly interconnected microstructure of Fe-rich and Cr-rich regions with a characteristic scale of several nanometers is formed. The knowledge of microstructural evolutions in the ferrite phase is important for the prediction of long-term stability of chemical reactors and the materials design of duplex stainless steels.

The atomic scale microstructures resulting from heat treatment of Fe–Cr binary alloys have been investigated by the Monte Carlo simulation.1,2) The computed atomic arrangement was reported to be in good agreement with those observed by position sensitive atom probe microanalysescite.2) The problems of the Monte Carlo method are the ambiguity in time scale for calculation and finite size effects.

In this paper, a numerical method based on the Cahn–Hilliard equation was applied for the simulation of phase separation. The Cahn–Hilliard nonlinear diffusion equation for binary alloy systems was extended to multicomponent system.3) The numerical simulations based on the Cahn–Hilliard equation were performed for Fe–Cr binary and Fe–Cr–Mo ternary alloys.

2. Method

2.1. The Cahn–Hilliard Equation for Multicomponent System

Since the average composition for an element $i$ in the total volume $V$.

$$
\bar{c}_i = \frac{1}{V} \int c_i(\vec{x}, t) d^3\vec{x}
$$

is conserved, the time-dependent concentration field $c_i(\vec{x}, t)$ satisfies a continuity equation.

$$
\frac{\partial c_i(\vec{x}, t)}{\partial t} + \nabla J_i(\vec{x}, t) = 0
$$

where $J_i(\vec{x}, t)$ is the concentration current density of the $i$ element. On the basis of non-equilibrium thermodynamics founded by Onsager, $J_i(\vec{x}, t)$ is proportional to the gradient of local chemical potential difference $\mu_i(\vec{x}, t)$:

$$
J_i(\vec{x}, t) = -M_i \nabla \mu_i(\vec{x}, t)
$$

where $M_i$ is the mobility of the $i$ element.

In a homogeneous alloy the difference in the chemical potential for the element $i$ is proportional to the partial derivative of the local free energy, $\partial f / \partial c_i$. In the presence of compositional fluctuation the quantity which is proportional to chemical potential is given by the functional derivative of the free energy with respect to composition.
Cahn and Hilliard showed the free energy of small volume of non uniform solution can be expressed as the sum of two contributions, the gradient energy and the local free energy $f_0(c)$ of homogenous solution. The free energy of inhomogeneous system of $N$-component system for a cubic lattice is given by:

$$f = \int f_0(c_1,\ldots, c_N) \frac{1}{2} \sum_{i,j} (K_{ij} \delta_{ij} + L_{ij}) \nabla c_i \nabla c_j \, dV$$

where $\delta_{ij}$ is the Kronecker’s delta and $K_{ij}$ and $L_{ij}$ are given by

$$K_i = -\frac{\partial^2 f}{\partial c_i \nabla^2 c_i} \bigg|_{c_0} + \frac{1}{2} \frac{\partial^2 f}{\partial |\nabla c_i|^2} \bigg|_{c_0}$$

$$L_{ij} = \frac{1}{2} \frac{\partial^2 f}{\partial (c_i \nabla c_j)} \bigg|_{c_0}$$

The subscript zero indicates the value of the parameter in a solution of uniform composition. Insertion Eqs. (3) and (5) in the continuity equation, one obtains the Cahn–Hilliard equation for multicomponent system.

$$\frac{\partial c_i(x, t)}{\partial t} = \nabla \cdot \left[ \nabla^2 (K_i c_i - K \nabla^2 c_i) + \sum_{j=1}^{N} L_{ij} \nabla^2 c_j \right]$$

We assume that contribution of terms $[\partial f/\partial |\nabla c_i|^2]_0$ and $[\partial f/\partial \nabla c_i \nabla c_j]_0$ for a regular solution are much smaller than that of $[\partial^2 f/\partial c_i \nabla c_i]_0$. Consequently we obtain

$$\frac{\partial c_i(x, t)}{\partial t} = \nabla \cdot \left[ \nabla^2 (K_i c_i - K \nabla^2 c_i) \right]$$

If the mobilities of elements are not dependent on their positions in the space, the above obtained Cahn–Hilliard Eq. (9) is reduced to a finite difference equation as

$$c_i(x, t + \Delta t) = c_i(x, t)$$

$$\frac{\partial c_i(x, t)}{\partial t} = \nabla \cdot \left[ \nabla^2 (K_i c_i - K \nabla^2 c_i) \right]$$

where $\sum_{NN}$ denotes the nearest neighbor interactions and is equivalent to the second derivative operator.

$$\sum_{NN} F(x, y, t) = F(x + \Delta x, y, t) + F(x - \Delta x, y, t) + F(x, y + \Delta y, t) + F(x, y - \Delta y, t) - 4F(x, y, t)$$

2.2. Evaluations of Mobilities and Gradient Energy Coefficients in Fe–Cr–Mo Ternary Alloys

In order to evaluate the mobility and the gradient energy-coefficient, Eq. (9) is linearized as

$$\mu(x, t) = \frac{\partial f}{\partial c_i}$$

$$\frac{\partial c_i(x, t)}{\partial t} = \frac{\partial^2 c_i}{\partial x^2} - M_i K_i \nabla^4 c_i$$

where the interdiffusion coefficient $\tilde{D}_i$ is related to

$$\tilde{D}_i = M_i \left( \frac{\partial f_0}{\partial c_i^2} \right)$$

With use of the regular solution model, the local free energy $f_0$ is written as

$$f_0 = f_0(1 - c_{Cr} - c_{Mo}) + f_{Cr} c_{Cr} + f_{Mo} c_{Mo}$$

$$+ \Omega_{FeCr} c_{Cr} (1 - c_{Cr} - c_{Mo}) + \Omega_{FeMo} c_{Mo} (1 - c_{Cr} - c_{Mo})$$

$$+ \nabla \cdot (\nabla f_0 c_{Cr} + c_{Cr} \nabla c_{Cr})$$

where $R$ is the gas constant, $T$ is the absolute temperature, $\Omega_{FeCr}$, $\Omega_{FeMo}$ and $\Omega_{CrMo}$ are interaction parameters, and $f_{Cr}$, $f_{Mo}$, and $f_{CrMo}$ are the molar free energy of pure Fe, pure Cr and pure Mo, respectively. Substituting Eq. (14) into Eq. (13), one obtains the mobilities and the free energy coefficients for Fe–Cr–Mo ternary alloys as

$$M_{Cr} = \frac{D_{Cr}}{2 \Omega_{FeCr} - 4RT}$$

$$M_{Mo} = \frac{D_{Mo}}{2 \Omega_{FeMo} - 4RT}$$

$$K_{Cr} = \frac{1}{6} \times (\text{lattice constant})^2 \times \Omega_{FeCr}$$

$$K_{Mo} = \frac{1}{6} \times (\text{lattice constant})^2 \times \Omega_{FeMo}$$

where $D_{Cr}$ is the diffusion coefficient of Cr in Fe–50at%Cr steel and $D_{Mo}$ is the diffusion coefficient of Mo in Fe–50at%Mo steel. The following values for $D_{Cr}$ and $D_{Mo}$ were used for the present simulation. 5)

$$D_{Cr} = 0.19 \times \exp \left( \frac{-246000}{RT} \right) \times c_i$$

$$D_{Mo} = 0.29 \times \exp \left( \frac{-266000}{RT} \right) \times c_i$$

where constant $c_i$ in Eqs. (19)–(20) is an adjustable parameter which varies within the range that the above values do not exceed experimental error bars. The constant $c_i = 0.01$ was used in the present simulation. The regular solution model was applied to the evaluation of the free energy. Table 1 shows the interaction parameters $\Omega_{ij}$ used for

| Interaction parameter $\Omega_{ij}$ | $kJ/mol$ |
|-----------------------------------|---------|
| $\Omega_{FeCr}$                  | 18.6    |
| $\Omega_{CrMo}$                  | 18.2    |
| $\Omega_{CrMo}$                  | 8.0     |
Numerical simulations were executed for Fe–Cr binary alloys and Fe–Cr–Mo ternary alloys in the temperature range between 750–800 K. Temporal and spatial evolutions of Cr and Mo concentration in the 2-dimensional region with an area of 30 nm² were simulated by the model. Periodic boundary condition was applied.

3. Results and Discussions

3.1. Fe–Cr Binary Alloys

Figure 1 shows temporal evolutions of the counter map of the Cr concentration in an Fe–40at%Cr binary alloy aged at 800 K. Although the initial fluctuation of the Cr concentration seems to be damped out with aging time, the formation of Cr rich regions by phase separation is clearly seen in this figure. The size and interdistance are increased with aging time. A modulated structure with wave length of about 4 nm is created at aging time of 200 hr. This is in good agreement with the reported experimented result. The variation of concentration profiles of Cr is shown in Fig. 2. The peak of the amplitude is equivalent to the equilibrium concentration of Cr at 800 K, which is evaluated by Thermo–Calc.

3.2. Fe–Cr–Mo Ternary Alloys

Temporal evolutions of counter maps of Cr and Mo concentration in an Fe–40at%Cr–3at%Mo ternary alloy at 800 K are shown in Figs. 3 and 4. The initial fluctuations of the Cr and Mo concentrations seem to be damped out with aging time. The formations of the Cr and Mo rich regions by phase separation are observed in these figures. The wavelength of the Cr rich regions at aging time of 200 hr. is about 4 nm, which is similar to that of Mo rich region. It seems that the addition of Mo has no significant influence on the diffusion coefficient. However this is not clear because the cross term in Eq. (5) is neglected in the present simulation. Figure 5 shows the variation in the concentration profile of Cr together with that of Mo. The Mo rich regions are formed inside the Cr rich regions. However a little decrease in the amplitude of Mo concentration is observed at the peak positions of Cr.

Mechanism of the formation of the above microstructure is as follows: The periodic structure which include high amount of Cr and Mo is formed by phase separation due to the strong repulsive interactions of Fe–Cr and Fe–Mo. Interaction parameter of Cr and Mo in Fe–Cr–Mo ternary alloys, \( W_{\text{CrMo}} \), is written as

\[
W_{\text{CrMo}} = \Omega_{\text{CrMo}} - \Omega_{\text{FeCr}} - \Omega_{\text{FeMo}} \quad \text{(21)}
\]

The value of \( W_{\text{CrMo}} \) by Eq. (21) is \(-28.8\) kJ/mol. This means that Cr–Mo pair is more stable than Fe–Cr and Fe–Mo pairs. However, because of the repulsive interaction of Cr and Mo, a valley of the amplitude of Mo concentration is formed at the peak positions of Cr concentration.

Fig. 1. Temporal evolution of Cr concentration counter map in Fe–40at%Cr binary alloy at 800 K.

Fig. 2. Variation of Cr concentration profile with time in Fe–40at%Cr binary alloy at 800 K.
3.3. Effect of Aging Temperature on Phase Separation

Figures 6 and 7 show concentration profile of Cr in the Fe–40at%Cr binary alloy at 775 K and 750 K respectively. The growth rate of the amplitude becomes slower with decrease in aging temperature. The effect of aging temperature on the wavelength of Cr concentration fluctuation after aging for 200 hr. is shown in Fig. 8. The wavelength nearly linearly increases with aging temperature. The wavelength of Cr concentration profile at 800 K is about twice as that at 750 K.

Let us analyse the above result by the linearized Cahn–Hilliard Equation. Expanding the atomic concentration into Fourier series, Eq. (12) can be written as

\[
\frac{\partial A(\vec{k})}{\partial t} = R(\vec{k})A(\vec{k}) \quad \cdots \cdots \cdots (22)
\]

with the amplitude

\[
A(\vec{k}) = \int \delta c(\vec{x}, t) \exp(i\vec{k} \cdot \vec{x}) d\vec{x} \quad \cdots \cdots \cdots (23)
\]

of a Fourier component with the wave number \(k = 2\pi/\lambda\) if \(\lambda\) denotes the wavelength of composition. A fluctuation of concentration is written as

\[A(\vec{k}) \approx \delta c(\vec{x}, t) \exp(i\vec{k} \cdot \vec{x})\]
\[ \delta c(x, t) = c(x, t) - c_0 \] ........................(24)

where \(c_0\) is the bulk composition. Equation (22) is solved by a simple exponential relation,

\[ \delta c(x, t) = \delta c_0 \exp[R(\vec{K})t] \] ........................(25)

where \(\delta c_0\) is a fluctuation at time 0 and \(R(\vec{K})\) is

\[ R(\vec{K}) = -Mk^2 \left( \frac{\partial^2 f}{\partial c^2} \right) + Kk^2 \] ........................(26)

Thus \(R(\vec{K})\) is position for \(0 < k < k_0\) with

\[ k_0 = \frac{2\pi}{\lambda_c} = \left[ -\frac{\partial^2 f_0}{\partial c^2} / K \right]^{1/2} \] ........................(27)

or, respectively for all fluctuation wavelength \(\lambda\) larger than \(\lambda_c\) which is given by,

\[ \lambda = \frac{2\pi}{\lambda_c} = \frac{2\pi k^{1/2}}{\Omega_{FeCr} - RT \left[ \frac{1}{c} + \frac{1}{1 - c} \right]} \] ........................(28)

From Eq. (28) \(\lambda\) decreases with decrease in aging temperature. However, the \(\lambda_c\) at 750 K estimated by Eq. (28) is only about 10% smaller than that at 800 K. This indicated that decrease in the wavelength may be due the nonlinear term of the Cahn–Hilliard Equation.
4. Summary

The Cahn–Hilliard nonlinear equation for binary alloy system was extended to multicomponent systems. Numerical model based on the Cahn–Hilliard equation for multicomponent system was applied to prediction of microstructural evolutions in Fe–Cr binary and Fe–Cr–Mo ternary alloys. The free energy of the system was approximated by the regular solution model. The following results are obtained.

(1) In an Fe–40at%Cr binary alloy, the Cr composition profile at 800 K shows a modulated structure with the wavelength of 4 nm. These results are consistent with those of Atom-probe FIM analyses reported in the literature.

(2) In an Fe–40at%Cr–3at%Mo ternary alloy, the wavelength of Cr and Mo composition profiles were similar to that for the binary alloys.

(3) However, the decrease in Mo composition was observed at the peak position of Cr composition because of the repulsive interaction of Cr and Mo atoms.

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