Effect of Mo on Phase Separation in Fe-40 at% Cr Alloys Based on Numerical Solutions of the Cahn Hilliard Equation

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Effect of Mo on phase separation behavior of Cr in Fe-40 at%Cr-Mo ternary alloys was investigated with use of a model based on the Cahn-Hilliard eqaution. Simulation result indicates that the addition of a small amount of Mo to an Fe-40 at%Cr binary alloy was found to accelerate phase separation. With addition of small amount of Mo up to 5 at%, the rate of phase separtion concentration of Cr along the trajectory of its peak top increases with time. Mechanism of this acceleration behavior of Cr was analyzed by using a theory on asymptotic behavior of substitutional element in ternary alloy proposed by the present authors.   [doi:10.2320/matertrans.MRA2006335]

1. Introduction

Control of microstructural evolutions associated with phase separation is important for materials design of Fe-based alloys. Nanoscale 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.[1]

Behavior of phase separation in ternary alloys[2] is known to be different from that of binary alloys. According to numerical simulations of phase separation in Fe-Cr binary and Fe-Cr-Mo ternary alloys by Suwa and Saito,[3] the addition of Mo to the Fe-Cr binary alloys accelerates decomposition. Figure 1 shows variations in the average areas of the Cr-rich phases in an Fe-40 at%Cr binary alloy and an Fe-40 at%Cr-5 at%Mo ternary alloy with time. This figure indicates that the decomposition of Cr in the ternary alloy is faster than that in the binary alloy. The Monte Carlo simulation result[4] of phase separation in Fe-Cr-Mo ternary alloys indicates that the decreasing rate in the number of Fe-Cr pairs, which is closely related to the rate of phase separation, in the Fe-40 at%Cr-5 at%Mo ternary alloy is higher than that in the Fe-40 at%Cr binary alloy.

This paper deals with asymptotic behavior of Cr in Fe-Cr-Mo ternary alloys induced by the addition of Mo to an Fe-40 at%Cr binary alloy. Mechanism for acceleration of phase separation is investigated by using a theory on asymptotic behavior of substitutional elements in ternary alloys proposed by the present authors.[5]

2. Model

2.1 The Cahn-Hilliard equation for an Fe-Cr-Mo alloy

We consider one-dimentional case for simplicity. If the mobilities of Cr and Mo, M_{Cr} and M_{Mo} are not dependent on their positions in the space, the Cahn-Hillirad equation for an Fe-Cr-Mo ternary alloy is given by[6–8]
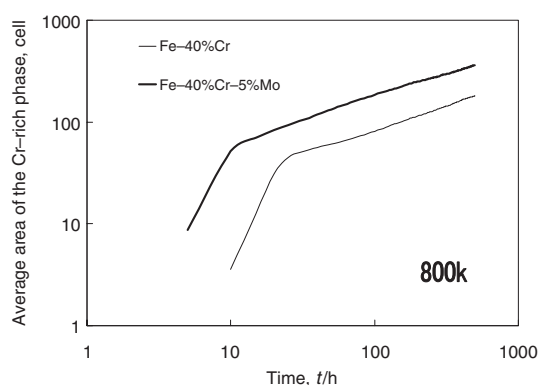

Fig. 1 Variations in the average areas of the Cr-rich phases in an Fe-40 at%Cr binary alloy and an Fe-40 at%Cr-5 at%Mo ternary alloy with time.[3]

$$\frac{\partial c_{Cr}}{\partial t} = M_{Cr}\left[\frac{\partial^2}{\partial x^2}\left(\frac{\partial f'}{\partial c_{Cr}} - K_{Cr}\frac{\partial^2 c_{Cr}}{\partial x^2} - L_{CrMo}\frac{\partial^2 c_{Mo}}{\partial x^2}\right)\right] \quad (1)$$

$$\frac{\partial c_{Mo}}{\partial t} = M_{Mo}\left[\frac{\partial^2}{\partial x^2}\left(\frac{\partial f'}{\partial c_{Mo}} - L_{CrMo}\frac{\partial^2 c_{Cr}}{\partial x^2} - K_{Mo}\frac{\partial^2 c_{Mo}}{\partial x^2}\right)\right] \quad (2)$$

where $c_{Cr}(x, t)$ and $c_{Mo}(x, t)$ are concentration fields of Cr and Mo elements, respectively, f' is the local free energy and K_{Cr}, K_{Mo} and L_{CrMo} are gradient energy coefficients. Equations (1) and (2) yield

$$\frac{\partial c_{Cr}}{\partial t} = M_{Cr}\left[\frac{\partial^2 f'}{\partial c_{Cr}^2}\frac{\partial^2 c_{Cr}}{\partial x^2} + \frac{\partial^2 f'}{\partial c_{Cr}\partial c_{Mo}}\frac{\partial^2 c_{Mo}}{\partial x^2}\right.$$
$$+ 2\frac{\partial^3 f'}{\partial c_{Cr}^2 \partial c_{Mo}}\frac{\partial c_{Cr}}{\partial x}\frac{\partial c_{Mo}}{\partial x} + \frac{\partial^3 f'}{\partial^3 c_{Cr}}\left(\frac{\partial c_{Cr}}{\partial x}\right)^2$$
$$\left. + \frac{\partial^3 f'}{\partial c_{Cr}\partial^2 c_{Mo}}\left(\frac{\partial c_{Mo}}{\partial x}\right)^2 - K_{Cr}\frac{\partial^4 c_{Cr}}{\partial x^4} - L_{CrMo}\frac{\partial^4 c_{Mo}}{\partial x^4}\right]$$
$$\quad (3)$$

$$\frac{\partial c_{Mo}}{\partial t} = M_{Mo}\left[\frac{\partial^2 f'}{\partial c_{Cr}\partial c_{Mo}}\frac{\partial^2 c_{Cr}}{\partial x^2} + \frac{\partial^2 f'}{\partial c_{Mo}^2}\frac{\partial^2 c_{Mo}}{\partial x^2}\right.$$

$$+ 2\frac{\partial^3 f'}{\partial c_{Cr}\partial c_{Mo}^2}\frac{\partial c_{Cr}}{\partial x}\frac{\partial c_{Mo}}{\partial x} + \frac{\partial^3 f'}{\partial c_{Cr}^2\partial c_{Mo}}\left(\frac{\partial c_{Cr}}{\partial x}\right)^2$$

$$\left. + \frac{\partial^3 f'}{\partial c_{Mo}^3}\left(\frac{\partial c_{Mo}}{\partial x}\right)^2 - L_{CrMo}\frac{\partial^4 c_{Cr}}{\partial x^4} - K_{Mo}\frac{\partial^4 c_{Mo}}{\partial x^4}\right] \quad (4)$$

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

$$f' = f_{Fe}(1 - c_{Cr} - c_{Mo}) + f_{Cr}c_{Cr}$$
$$+ f_{Mo}c_{Mo} + \Omega_{FeCr}c_{Cr}(1 - c_{Cr} - c_{Mo})$$
$$+ \Omega_{FeMo}c_{Mo}(1 - c_{Cr} - c_{Mo}) + \Omega_{CrMo}c_{Cr}c_{Mo}$$
$$+ RT[(1 - c_{Cr} - c_{Mo})\ln(1 - c_{Cr} - c_{Mo})$$
$$+ c_{Cr}\ln c_{Cr} + c_{Mo}\ln c_{Mo}] \quad (5)$$

where R is the gas constant, T is the absolute temperature, Ω_{FeCr}, Ω_{FeMo} and Ω_{CrMo} are interaction parameters and f_{Fe}, f_{Cr} and f_{Mo} are the molar free energies of pure Fe, pure Cr and pure Mo, respectively. From eq. (5) it follows that

$$\frac{\partial^2 f'}{\partial c_{Cr}^2} = -2\Omega_{FeCr} + RT\left(\frac{1}{c_{Cr}} + \frac{1}{1 - c_{Cr} - c_{Mo}}\right) \quad (6)$$

$$\frac{\partial^2 f'}{\partial c_{Mo}^2} = -2\Omega_{FeMo} + RT\left(\frac{1}{c_{Mo}} + \frac{1}{1 - c_{Cr} - c_{Mo}}\right) \quad (7)$$

$$\frac{\partial^2 f'}{\partial c_{Cr}\partial c_{Mo}} = \Omega_{CrMo} - \Omega_{FeCr} - \Omega_{FeMo} + \frac{RT}{1 - c_{Cr} - c_{Mo}} \quad (8)$$

2.2　Conditions of numerical simulations

Numerical simulations based on the Cahn-Hilliard Equation were performed for Fe-40 at%Cr-Mo ternary alloys. Concentration of Mo varies between 0 to 15 at%. The mobilities and the gradient energy coefficients for Fe-Cr-Mo ternary alloys are[6]

$$M_{Cr} = \frac{c_1 \cdot D_{Cr}}{2\Omega_{FeCr} - 4RT}, \quad M_{Mo} = \frac{c_1 \cdot D_{Mo}}{2\Omega_{FeMo} - 4RT} \quad (9)$$

$$K_{Cr} = \frac{1}{2} \cdot a_0^2 \cdot \Omega_{FeCr}, \quad K_{Mo} = \frac{1}{2} \cdot a_0^2 \cdot \Omega_{FeMo} \quad (10)$$

$$L_{CrMo} = L_{CrMo} = \frac{1}{2} \cdot a_0^2(\Omega_{CrMo} - \Omega_{FeCr} - \Omega_{FeMo}) \quad (11)$$

where a_0 is the lattice constant, D_{Cr} is the diffusion coefficient of Cr in Fe-50 at%Cr alloy and D_{Mo} is the diffusion coefficient of Mo in Fe-50 at%Mo alloy. The following values for D_{Cr}, and D_{Mo} were used for simulation.[9,10]

$$D_{Cr} = 0.19\exp\left(-\frac{246000}{RT}\right) \quad (12)$$

$$D_{Mo} = 0.29\exp\left(-\frac{264000}{RT}\right) \quad (13)$$

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.[11] The constant 0.01 for c_1 was used in the present simulation. The interaction parameters are[12]
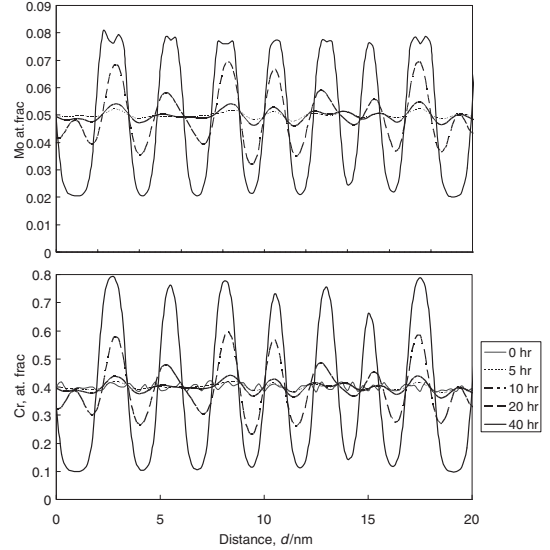

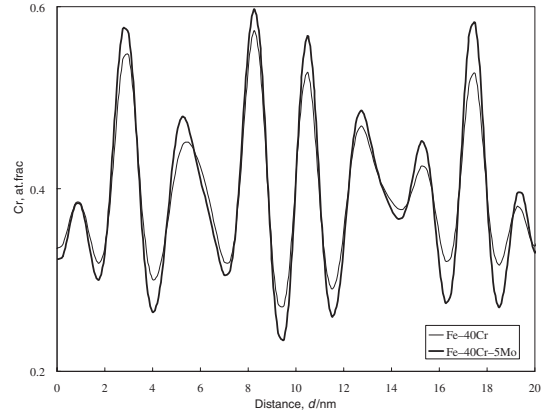Fig. 2　Variation in the concentration profiles of Cr and Mo in an Fe-40 at%Cr-5 at%Mo alloy.

Fig. 3　Cr Concentration profiles of Fe-40 at%Cr binary alloy and Fe-40 at%Cr-5 at%Mo ternary alloy aged at 800 K for 20 h.

$$\Omega_{FeCr} = 18.6\,\text{kJ/mol}, \quad \Omega_{FeMo} = 18.2\,\text{kJ/mol},$$
$$\Omega_{CrMo} = 8.0\,\text{kJ/mol}. \quad (14)$$

3.　Result and Discussion

3.1　Effect of Mo on Phase Separation Behavior of Cr

Numerical simulations based on the Cahn-Hilliard Equation were performed for Fe-40 at%Cr-Mo ternary alloys. Concentration of Mo varies between 0 to 15 at%.

Variation in the concentration profiles of Cr and Mo in an Fe-40 at%Cr-5 at%Mo alloy is shown in Fig. 2. 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. At the later stage of phase separation the bifurcation of Mo peaks are observed.

Figure 3 describes Cr concentration profiles of Fe-40 at%Cr binary alloy and Fe-40 at%Cr-5 at%Mo ternary alloy aged at 800 K for 20 h. It is shown that the addition of Mo accelerates decomposition at the initial stage of spinodal decomposition.
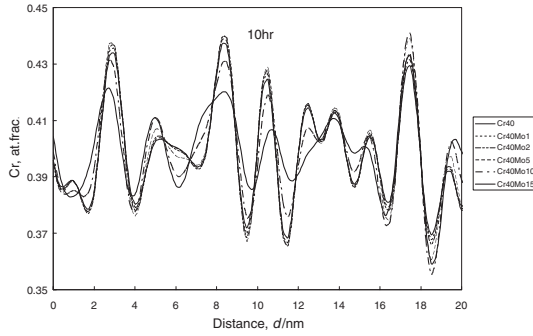
Fig. 4 Concentration profiles of Cr in Fe-40 at%Cr-Mo ternary alloys with 0 to 15 at%Mo aged at 800 K for 10 h.
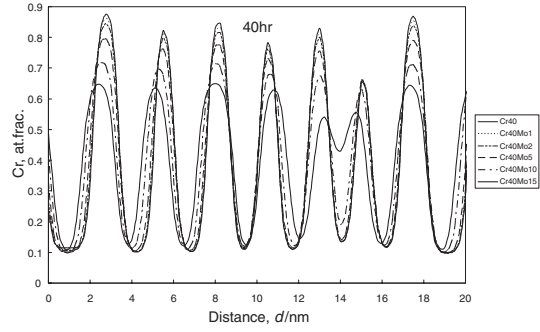

Fig. 6 Concentration profiles of Cr in Fe-40 at%Cr-Mo ternary alloys with 0 to 15 at%Mo aged at 800 K for 40 h.
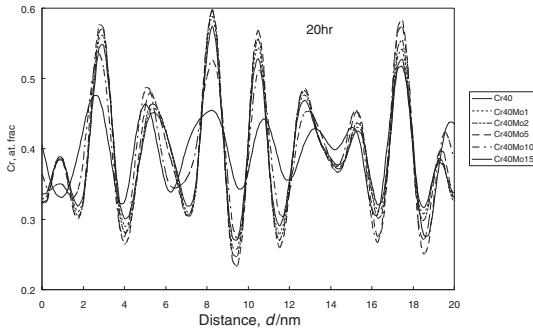

Fig. 5 Concentration profiles of Cr in Fe-40 at%Cr-Mo ternary alloys with 0 to 15 at%Mo aged at 800 K for 20 h.
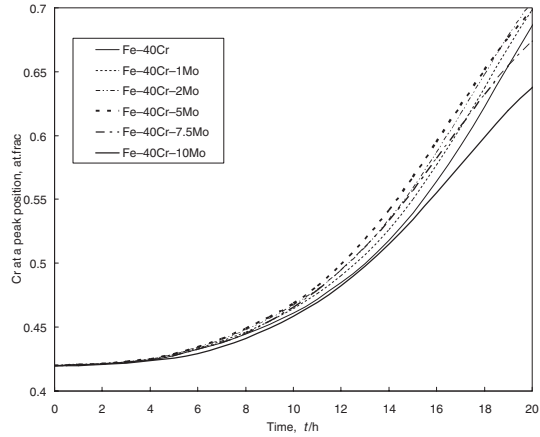

Fig. 7 Variations in peak heights of Cr in Fe-40 at%Cr-Mo ternary alloys with 0 to 10 at% Mo accompanying phase separation.

Concentration profiles of Cr in Fe-40 at%Cr-Mo ternary alloys with 0 to 15 at%Mo aged at 800 K for 10 h are shown in Fig. 4. The accreration of phase separation with addition of Mo is small in this period. However, as shown in Fig. 5, the addition of Mo up to 5 at% increases peak height of Cr peaks at aging time of 20 h. It indicates that velocity of phase decomposition is increases with increase of Mo if Mo concentration is up to 5 at%. With the addition of Mo higher than 10 at% delays decomposition of Cr. Figure 6 shows concentration profiles of Cr in Fe-40 at%Cr-Mo ternary alloys with 0 to 15 at% Mo aged at 800 K for 40 h. Although areas of Cr rich regions are increased peak heights of Cr peaks decreases with addition of Mo. This implys that the addition of Mo delays phase separation of Cr in Fe-40 at%Cr-Mo ternary alloys.

Variations in peak heights of Cr in Fe-40 at%Cr-Mo ternary alloys accompanying phase separation are shown in Fig. 7. Acceleration of phase decomposition with addition of Mo at the initial stage and the slow down at the later stage is shown in this Figure.

3.2 Asymptotic Behavior of Cr and Mo in Fe-Cr-Mo Ternary Alloys

In order to analyze the effect of Mo on phase separation behavior in Fe-Cr-Mo ternary alloys, we deal with asymptotic behavior of the Cr and Mo at peaks of c_{Cr} with use of eqs. (3) and (4) Functions G_{Cr} and G_{Mo} are difined as

$$G_{Cr}\left(t, x, c_{Cr}, c_{Mo}, \frac{\partial c_{Cr}}{\partial x}, \frac{\partial c_{Mo}}{\partial x}, \frac{\partial c_{Cr}^2}{\partial x^2}, \frac{\partial c_{Mo}^2}{\partial x^2}, \frac{\partial^4 c_{Cr}}{\partial x^4}, \frac{\partial^4 c_{Mo}}{\partial x^4}\right) \equiv M_{Cr}\left[\frac{\partial^2 f'}{\partial c_{Cr}^2}\frac{\partial^2 c_{Cr}}{\partial x^2} + \frac{\partial^2 f'}{\partial c_{Cr}\partial c_{Mo}}\frac{\partial^2 c_{Mo}}{\partial x^2}\right.$$
$$\left. + 2\frac{\partial^3 f'}{\partial c_{Cr}^2 \partial c_{Mo}}\frac{\partial c_{Cr}}{\partial x}\frac{\partial c_{Mo}}{\partial x} + \frac{\partial^3 f'}{\partial c_{Cr}^3}\left(\frac{\partial c_{Cr}}{\partial x}\right)^2 + \frac{\partial^3 f'}{\partial c_{Cr}\partial^2 c_{Mo}}\left(\frac{\partial c_{Mo}}{\partial x}\right)^2 - K_{Cr}\frac{\partial^4 c_{Cr}}{\partial x^4} - L_{CrMo}\frac{\partial^4 c_{Mo}}{\partial x^4}\right] \tag{15}$$

$$G_{Mo}\left(t, x, c_{Cr}, c_{Mo}, \frac{\partial c_{Cr}}{\partial x}, \frac{\partial c_{Mo}}{\partial x}, \frac{\partial^2 c_{Cr}}{\partial x^2}, \frac{\partial^2 c_{Mo}}{\partial x^2}, \frac{\partial^4 c_{Cr}}{\partial x^4}, \frac{\partial^4 c_{Mo}}{\partial x^4}\right) \equiv M_{Mo}\left[\frac{\partial^2 f'}{\partial c_{Cr}\partial c_{Mo}}\frac{\partial^2 c_{Cr}}{\partial x^2} + \frac{\partial^2 f'}{\partial c_{Mo}^2}\frac{\partial^2 c_{Mo}}{\partial x^2}\right.$$
$$\left. + 2\frac{\partial^3 f'}{\partial c_{Cr}\partial c_{Mo}^2}\frac{\partial c_{Cr}}{\partial x}\frac{\partial c_{Mo}}{\partial x} + \frac{\partial^3 f'}{\partial c_{Cr}^2 \partial c_{Mo}}\left(\frac{\partial c_{Cr}}{\partial x}\right)^2 + \frac{\partial^3 f'}{\partial c_{Mo}^3}\left(\frac{\partial c_{Mo}}{\partial x}\right)^2 - L_{CrMo}\frac{\partial^4 c_{Cr}}{\partial x^4} - K_{Mo}\frac{\partial^4 c_{Mo}}{\partial x^4}\right] \tag{16}$$

These functions satisfy the following conditions:

$$G_{Cr}\left(t, x_p, c_{Cr}, c_{Mo}, 0, \frac{\partial c_{Mo}}{\partial x}, 0, \frac{\partial^2 c_{Mo}}{\partial x^2}, \frac{\partial^4 c_{Cr}}{\partial x^4}, \frac{\partial^4 c_{Mo}}{\partial x^4}\right) =$$

$$M_{Cr}\left[\frac{\partial^2 f'}{\partial c_{Cr}\partial c_{Mo}}\frac{\partial^2 c_{Mo}}{\partial x^2} + \frac{\partial^3 f'}{\partial c_{Cr}\partial c_{Mo}^2}\left(\frac{\partial c_{Mo}}{\partial x}\right)^2 - K_{Cr}\frac{\partial^4 c_{Cr}}{\partial x^4} - L_{CrMo}\frac{\partial^4 c_{Mo}}{\partial x^4}\right] \tag{17}$$

$$G_{Mo}\left(t, x_p, c_{Cr}c_{Mo}, 0, \frac{\partial c_{Mo}}{\partial x}, 0, \frac{\partial^2 c_{Mo}}{\partial x^2}, \frac{\partial^4 c_{Cr}}{\partial x^4}, \frac{\partial^4 c_{Mo}}{\partial x^4}\right) =$$

$$M_{Mo}\left[\frac{\partial^2 f'}{\partial c_{Mo}^2}\frac{\partial^2 c_{Mo}}{\partial x^2} + \frac{\partial^3 f'}{\partial c_{Mo}^3}\left(\frac{\partial c_{Mo}}{\partial x}\right)^2 - L_{CrMo}\frac{\partial^4 c_{Cr}}{\partial x^4} - K_{Mo}\frac{\partial^4 c_{Mo}}{\partial x^4}\right] \tag{18}$$

At a peak position $p(x_p, t)$

$$\frac{\partial c_{Cr}}{\partial x} = 0 \quad \frac{\partial^2 c_{Cr}}{\partial x^2} < 0 \tag{19}$$

Applying the mean value theorem of differential calculus for compound fuction,[13] we obtain the following equation for an intermediate value ζ in the open interval $(\partial^2 c_{Cr}/\partial x^2, 0)$

$$\frac{dc_{Cr}}{dt}(x_p, t) = M_{Cr}\left[\frac{\partial^2 f'}{\partial c_{Cr}^2}\frac{\partial^2 c_{Cr}}{\partial x^2}(\zeta, t) + \frac{\partial^2 f'}{\partial c_{Cr}\partial c_{Mo}}\frac{\partial^2 c_{Mo}}{\partial x^2} + \frac{\partial^3 f'}{\partial c_{Cr}\partial c_{Mo}^2}\left(\frac{\partial c_{Mo}}{\partial x}\right)^2\right.$$

$$\left. - K_{Cr}\frac{\partial^4 c_{Cr}}{\partial x^4} - L_{CrMo}\frac{\partial^4 c_{Mo}}{\partial x^4}\right] \tag{20}$$

$$\frac{dc_{Mo}}{dt}(x_p, t) = M_{Mo}\left[\frac{\partial^2 f'}{\partial c_{Cr}\partial c_{Mo}}\frac{\partial^2 c_{Cr}}{\partial x^2}(\zeta, t) + \frac{\partial^2 f'}{\partial c_{Mo}^2}\frac{\partial^2 c_{Mo}}{\partial x^2} + \frac{\partial^3 f'}{\partial c_{Mo}^3}\left(\frac{\partial c_{Mo}}{\partial x}\right)^2\right.$$

$$\left. - L_{CrMo}\frac{\partial^4 c_{Cr}}{\partial x^4} - K_{Mo}\frac{\partial^4 c_{Mo}}{\partial x^4}\right] \tag{21}$$

Here we consider the case in which the concentration of Cr in an Fe-Cr-Mo ternary alloy, c_{Cr} and c_{Mo} satisfy the following conditions

$$c_{Cr} > c_{Mo}, \quad \frac{\partial^2 f'}{\partial c_{Cr}^2} < 0, \quad \frac{\partial^2 f'}{\partial c_{Mo}^2} > 0 \tag{22}$$

The mechanism for bifurcation formation of peaks can be explained by a theory proposed by the present authors.[5,6] Equation (21) along a peak top of c_{Cr} can be approximated by

$$\frac{dc_{Mo}}{dt} \approx M_{Mo}\frac{\partial^2 f'}{\partial c_{Cr}c_{Mo}}\frac{\partial^2 c_{Cr}}{\partial x^2} \tag{23}$$

From eq. (23) it is indicated that the behavior of Mo at a peak position of Cr depends on the sign of $f'_{CrMo} \equiv \partial^2 f'/\partial c_{Cr}\partial c_{Mo}$. The sign of f'_{CrMo} may change from negative to positive in lower temperatures at which the equilibrium concentration of Cr is high. This indicates that bifurcation of peaks will occur at the later stage of phase decomposition as shown in Fig. 2.

Now let us consider asymptotic behavior of Cr at peak tops of c_{Cr}. Once peaks or bottoms of c_{Mo} form at peak tops of c_{Cr}, the third term of eq. (20) is zero. The fourth order derivative terms attribute to the interfacial energies of Cr and Mo in the Fe matrix. The contribution of these terms at the peaks of c_{Cr} is assumed to be smaller than the first and the second terms. Then at peaks of c_{Cr}, eq. (20) can be approximated by

$$\frac{dc_{Cr}}{dt}(x_p, t) \simeq M_{Cr}\left[\frac{\partial^2 f'}{\partial c_{Cr}^2}\frac{\partial^2 c_{Cr}}{\partial x^2} + \frac{\partial^2 f'}{\partial c_{Cr}\partial c_{Mo}}\frac{\partial^2 c_{Mo}}{\partial x^2}\right] \tag{24}$$

The sign of $f'_{CrCr} \equiv \partial^2 f'/\partial c_{Cr}^2$ is negative within the spinoal region. The values of f'_{CrCr} and $f'_{CrMo} \equiv \partial^2 f'/\partial c_{Cr}\partial c_{Mo}$ are given by eqs. (6) and (8), respectively. The first term in the right hand side of eq. (24) describes the phenomena of uphill diffusion, which is the major feature of phase decomposition in binary alloys. The second term represents the effect of Mo on variation in c_{Cr} induced by the addition of Mo.

From eq. (8), if the effect of Mo on the term $\partial^2 c_{Cr}/\partial x^2$ in eq. (24)is neglected, from eqs. (6), (8) and (24) the variation of dc_{Cr}/dt with addition of Mo is approximated by an equation

$$\left[\frac{dc_{Cr}}{dt}(x_p, t)\right]_{Fe-Cr-Mo} - \left[\frac{dc_{Cr}}{dt}(x_p, t)\right]_{Fe-Cr}$$

$$\simeq M_{Cr}RT\left[\left(\frac{1}{1 - c_{Cr} - c_{Mo}} - \frac{1}{1 - c_{Cr}}\right)\frac{\partial^2 c_{Cr}}{\partial x^2}\right.$$

$$\left. + \frac{\partial^2 f'}{\partial c_{Cr}\partial c_{Mo}}\frac{\partial^2 c_{Mo}}{\partial x^2}\right] \tag{25}$$

Because of a strong repulsion between Fe and Cr atoms phase decomposition in an Fe-Cr binary alloy is initiated by a continous process at spinodal region. Variation of the peak top behavior of the Cr induced by the addition of a small amount of the Mo will be analyzed with use of eq. (24). Although there is a small decrease in the absolute value of f'_{CrCr}, the behavior of Cr is considered to be dominated by the second term in the right hand side of eq. (25). The interaction parameter of the Cr and Mo elements in an Fe-Cr-Mo ternary alloy is difined as

$$W_{CrMo} = \Omega_{CrMo} - \Omega_{FeCr} - \Omega_{FeMo} \qquad (26)$$

If the value of W_{CrMo} is negative and its absolute value is larger than RT/c_{Fe}, f'_{CrMo} is negative at the initial time. The amplitude of c_{Mo} along the peaks of c_{Cr} increases with time. Then peaks formation of c_{Mo} occur at peak positions of c_{Cr}. It follows that the sign of the second term in eq. (24) is positive. This accelerates decomposition. At a low temperature, the value of RT/c_{Fe} becomes larger than $|W_{CrMo}|$ at the later stage. Then the value of f'_{CrMo} changes from negative to positive and the bifurcation of peaks of c_{Mo} will occur. Because the signs of both $\partial^2 c_{Mo}/\partial x^2$ and f'_{CrMo} are positive, the positive sign of the second term will not change at the later stage. If the value of f'_{CrMo} is negative at the initial time, phase separation in Fe-Cr-Mo ternary alloys is accelerated by small addition of Mo.

With addition of large amount of Mo and/or with elapse of time, the absolute value of the first term(negative) in eq. (25) becomes larger, then phase separation of Cr is retarded.

The above discussion on the asymptotic behavior of Mo in Fe-40 at%Cr-Mo ternary alloy can be applicable to minor elements in ternary alloy systems such as Cr in Fe-40 at%Mo-Cr ternary alloys.

4. Conclusion

We proposed a mechanism for acceleration of phase separation induced by the addition of a small amount of Mo to an Fe-Cr binary alloy. The addition of Mo up to 5 at% to an Fe-40 at%Cr binary alloy accelerates phase decomposition at the intial stage. The second derivative of the chemical free energy, f', with respect to the concentrations of Cr and Mo, c_{Cr} and c_{Mo}, $f'_{CrMo} \equiv \partial^2 f'/\partial c_{Cr} \partial c_{Mo}$, controls behavior of the Mo along the trajectory of the peak top of c_{Cr} and peak top behavior of Cr. This mechanisms for acceleration of phase separation in Fe-Cr-Mo ternary alloys is due to the fact that there is a repulsive interaction between Cr and Mo.

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