JOURNAL OF MATERIALS SCIENCE 27 (1992) 2444–2448

Computer simulations of the phase decomposition on Cu–Co binary alloys based on the non-linear diffusion equation

T. MIYAZAKI, A. TAKEUCHI, T. KOYAMA
Department of Materials Science and Engineering, Nagoya Institute of Technology, Nagoya, Japan

Computer simulations of phase decomposition were performed for the Cu–Co alloy system on the basis of the non-linear diffusion equation. In the calculations, the modified regular solution approximation was adopted, i.e. the composition and temperature dependences of the interaction parameter, Ω, between the nearest neighbour atoms were taken into account and the mobility of atoms was defined as a function of solute composition. The phase decompositions were successfully computed for the Cu–Co alloys. The calculation method proposed here is applicable to many actual alloy systems.

1. Introduction

Theoretical investigations of the phase decomposition of supersaturated solid solution have been carried out by many researchers. Since Cahn and Hilliard [1, 2] proposed the non-linear diffusion equation in the 1960s, many researchers have attempted a theoretical analysis of phase decomposition on the basis of this equation [2–7]. Cahn [4], assuming the interdiffusion coefficient, $\tilde{D}$, to be independent of composition, derived the well-known linear theory of spinodal decomposition. Cahn's analysis introduced the amplification factor and announced the concept of the predominant wave in the spinodal decomposition. This proposal has greatly contributed to the basic understanding of spinodal decomposition. However, the theory is only valid for the early stage of phase decomposition of the alloy, because of the neglect of the non-linear term in the diffusion equation. Since then, interest has moved to the precise evaluation of the non-linear term. Swanger *et al.* [5], Langer *et al.* [6] and Tsakalakos [7] analysed the phase decomposition process on the basis of such a point of view. However, various assumptions and omissions were made in their calculations, because it was extremely difficult to obtain an analytical solution of the non-linear part in the differential equation.

Tsujimoto [8–11] proposed the Fourier expression of the non-linear diffusion equation and devised a method by which the phase decomposition was precisely analysed. However, the calculation was only performed for a single composition peak formed at the origin of the coordinate axis. Our group [12, 13], having improved this method, succeeded in the computer simulations of various phase decompositions by using a polynomial free energy equation of solute composition and showed many interesting simulation results such as competitive growth among the composition peaks [12, 13], a reversion process of zones [14] and a spectrum behaviour of X-ray small-angle scattering with phase decomposition [14]. This method is considered to be very useful in the basic understanding of the phase decomposition process. Nevertheless, it was still difficult to apply the method for the actual alloy system, because the polynomial which was unsuitable for expressing the actual free energy was adopted in the calculation. Such a situation created a serious shortcoming in the practical use of this method.

However, recently we have proposed a new expression for the non-linear diffusion equation which was based on the regular solution approximation, and we have examined the propriety of the new method by computer simulation for a hypothetical phase diagram whose atomic interaction parameter, Ω, was independent of composition [15]. This method is applicable for the phase decomposition of the actual alloy systems which usually have a biasymmetric free energy curve with composition caused by the composition and temperature dependences of the atomic interaction parameter.

In the present work, taking into account the composition and temperature dependences of the interaction parameter, the computer simulations of phase decomposition for the Cu–Co binary alloy system were undertaken.

2. Calculation method

As the theoretical background has been presented in our previous paper [15], only the general calculation method for the Cu–Co alloy system is presented.

The non-linear diffusion equation of Cahn and Hilliard [1, 2], which expresses one-dimensional diffusion behaviour, is given by

$$\partial C_B/\partial t = \partial(\tilde{D}\partial C_B/\partial x)/\partial x - 2\partial(\tilde{K}\partial^3 C_B/\partial x^3)/\partial x \qquad (1)$$

The second term of the right-hand side of Equation 1 is an excess term of the chemical free energy, originating in the composition gradient. $\tilde{K}$ is the gradient energy coefficient. In order to perform the computer simulation of phase decomposition precisely, we must know the composition and temperature dependences of $\tilde{D}$ and $\tilde{K}$. Therefore, first we show the expressions for $\tilde{D}$ and $\tilde{K}$ for the Cu–Co alloy system, and then explain the Fourier expression of the non-linear flux equation.

2.1. Interdiffusion coefficient, $\tilde{D}$, and the gradient energy coefficient, $\tilde{K}$

The interdiffusion coefficient, $\tilde{D}$, and the gradient energy coefficient, $\tilde{K}$, are defined by Equations 2 and 3 [15].

$$\tilde{D} = M(C_B)(\partial^2 G/\partial C_B^2) \qquad (2)$$

$$\tilde{K} = M(C_B)\kappa(C_B, T) \qquad (3)$$

with $\kappa(C_B, T) = \kappa_0\{\Omega(C_B, T) + [\partial\Omega(C_B, T)/\partial C_B] C_B\}$, where $\kappa_0 = (r_0/3^{1/2})^2/2$, $\Omega(C_B, T)$ is the interaction parameter between atoms and r_0 shows a distance between the nearest neighbour atoms.

The chemical free energy, G, of the Cu–Co solid solution has been given by Nishizawa *et al.* [16].

$$G = \Omega(C_B, T)C_A C_B + RT(C_A \ln C_A + C_B \ln C_B) \qquad (4)$$

$$\Omega(C_B, T) = A_0(T) + A_1(T)(C_A - C_B) \qquad (5)$$

where $A_0(T) = 49\,500 - 13.32T$, $A_1(T) = 3575 - 0.9688\,T$, R is the gas constant and T is the absolute temperature. C_A and C_B are atomic concentrations of A and B atoms, respectively ($C_A + C_B = 1$).

The mobility, $M(C_B)$, in Equations 2 and 3 is defined by

$$M(C_B) = (M_A C_B + M_B C_A)C_A C_B \qquad (6)$$

where M_A and M_B are the mobilities of A and B atoms, respectively, which are related to the self diffusion coefficient, D_i^*, (i = A, B) by

$$D_i^* = M_i RT \qquad (7)$$

In the present calculation, M_A and M_B were assumed to be equal, for the simplification of calculation procedure, i.e.

$$M(C_B) = M_0 C_A C_B \quad (M_A = M_B \equiv M_0) \qquad (8)$$

By substituting Equations 4, 5 and 8 into Equations 2 and 3, we obtain expressions for the interdiffusion coefficient, $\tilde{D}$, and the gradient energy coefficient, $\tilde{K}$, for the Cu–Co alloy system.

$$\tilde{D} = D_0 + D_1 q(x,t) + D_2 q(x,t)^2 + D_3 q(x,t)^3 \qquad (9)$$

with

$$\begin{aligned} q(x,t) &\equiv C_B(x,t) - C_0 \\ D_0 &= -2M_0[A_0 C_A C_B + 3A_1(C_A - C_B)C_A C_B] + M_0 RT \\ D_1 &= -2M_0\{A_0(C_A - C_B) + 3A_1[(C_A - C_B)^2 - 2C_A C_B]\} \\ D_2 &= 2M_0[A_0 + 9A_1(C_A - C_B)] \\ D_3 &= -12M_0 A_1 \end{aligned}$$

$$\tilde{K} = K_0 + K_1 q(x,t) + K_2 q(x,t)^2 + K_3 q(x,t)^3 \qquad (10)$$

with

$$\begin{aligned} K_0 &= \kappa_0\{A_0 C_A C_B + A_1(C_A - 3C_B)C_A C_B\} \\ K_1 &= \kappa_0\{A_0(C_A - C_B) + A_1[(C_A - 3C_B)(C_A - C_B) - 4C_A C_B]\} \\ K_2 &= -\kappa_0[A_0 + A_1(5C_A - 7C_B)] \\ K_3 &= 4\kappa_0 A_1 \\ \kappa_0 &= [(r_0/3^{\frac{1}{2}})^2/2]M_0 \end{aligned}$$

$q(x, t)$ in Equation 9 shows a composition fluctuation from the average composition of alloy C_0 at location x. The diffusion coefficients D_0, D_1, D_2, D_3 and the gradient energy coefficients K_0, K_1, K_2 and K_3 of Equations 9 and 10 are single-valued functions of alloy composition, C_B.

2.2. A Fourier expression of the non-linear diffusion equation

The local deviation of solute composition from the average content $q(x, t)$ should be expressed as a Fourier series shown in Equation 11

$$q(x,t) = C_B(x,t) - C_0 = \sum_{h=-\infty}^{+\infty} Q_h(t)\exp(ih\beta x) \qquad (11)$$

where $Q_h(t)$ is an amplitude of a Fourier wave having the wave number h ($h = \pm 1, \pm 2, \ldots, h \neq 0$) at time t, and β is the reciprocal of length of the region considered, L, defined by $\beta = 2\pi/L$.

Substituting Equations 9, 10 and 11 for Equation 1 and rearranging Equation 1 we finally obtain a time dependence of $Q(h)$ [15]

$$\begin{aligned} \partial Q(h)/\partial t = &-(h\beta)^2[(D_0 + 2h^2\beta^2 K_0)Q_h] \\ &-(h\beta)^2[(1/2)D_1\phi_1(h) + (1/3)D_2\phi_2(h) + (1/4)D_3\phi_3(h)] \\ &-2h\beta^4[K_1\psi_1(h) + K_2\psi_2(h) + K_3\psi_3(h) \end{aligned} \qquad (12)$$

with

$$\phi_1(h) = \int Q(k)Q(h-k)\,\mathrm{d}k$$

$$\phi_2(h) = \int \phi_1(k)Q(h-k)\,\mathrm{d}k$$

$$\phi_3(h) = \int \phi_2(k)Q(h-k)\,\mathrm{d}k$$

$$\psi_1(h) = \int k^3 Q(k)Q(h-k)\,\mathrm{d}k$$

$$\psi_2(h) = \int \psi_1(k)Q(h-k)\,\mathrm{d}k$$

$$\psi_3(h) = \int \psi_2(k)Q(h-k)\,\mathrm{d}k$$

Where $\phi_1(h)$, $\phi_2(h)$ and $\phi_3(h)$ are the first, second and third convolutions of $Q(h)$, showing rates of synthesizing new waves. $\psi_1(h)$, $\psi_2(h)$ and $\psi_3(h)$ show the first, second and third convolutions of $Q(h)$ and $h^3Q(h)$. On the basis of Equation 12, we are able to calculate the time evolution of the Fourier components $Q(h)$ by repeating Equation 13

$$Q(h)_{t+\Delta t} = Q(h)_t + [\partial Q(h)/\partial t]_t \Delta t \qquad (13)$$

3. Calculation conditions

Fig. 1 shows the equilibrium phase diagram of Cu–Co alloy system calculated from Ω shown in Equations 4 and 5. The computer simulations were practiced for two alloys whose compositions are 50% and 20% Co at 1173 K, indicated by two solid circles in the figure.

The diffusion coefficients D_0, D_1, D_2 and D_3 in $\tilde{D}$ at 1173 K are shown in Fig. 2, and were evaluated in accordance with Equation 9. The alloy compositions where D_0 is zero coincide precisely with spinodal composition C_{sp1} and C_{sp2} at 1173 K of Fig. 1. The uphill diffusion caused by the D_0 term is expected to occur inside the spinodal composition, while the downhill diffusion ought to occur outside the composition.

Fig. 3 represents the composition dependences of K_0, K_1, K_2 and K_3 for the Cu–Co system at 1173 K, which were calculated from Equation 10. It should be noted that the composition dependences of each K term are just in inverse relation with that of the D terms shown in Fig. 2. These are considered to reflect that the interdiffusion coefficient, $\tilde{D}$, contributes to promote the phase decomposition, while the gradient energy coefficient, $\tilde{K}$, is concerned with the restraint force of phase decomposition. The phase decomposition seems to progress on the balance of the two forces.

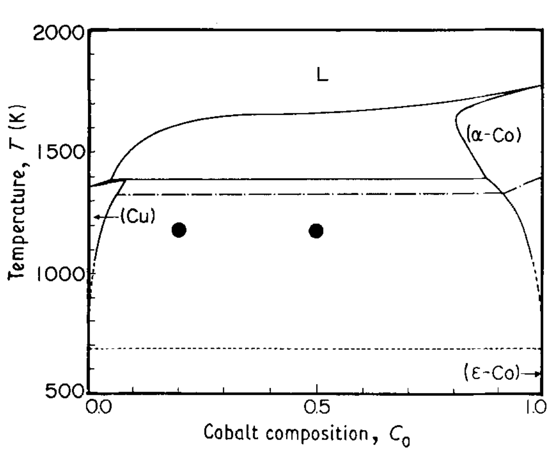

Figure 1 An equilibrium phase diagram of the Cu–Co alloy proposed by Hasebe and Nishizawa [16]: (●) at 1173 K show the chemical compositions for the computer simulations.

The extent of the wave number, h, during the calculation is restricted within ± 512 for convenience of computation. The wavelength of the shortest wave ($h = \pm 512$) is about 0.24 nm, which is less than the lattice constant of the typical alloys. The amplitude of the initial Fourier components and their signs are given at random.

Numerical values used for the calculation are summarized in Table I.

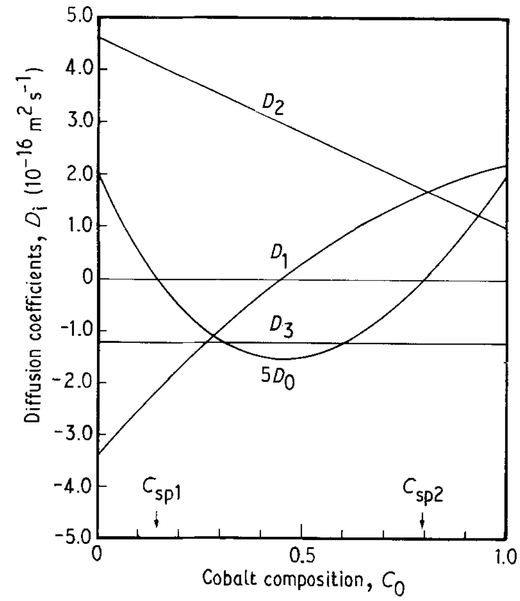

Figure 2 Changes in diffusion coefficients D_0, D_1, D_2 and D_3 with the average solute composition C_0 at 1173 K shown in Fig. 1. C_{sp1} and C_{sp2} show the spinodal compositions at 1173 K.

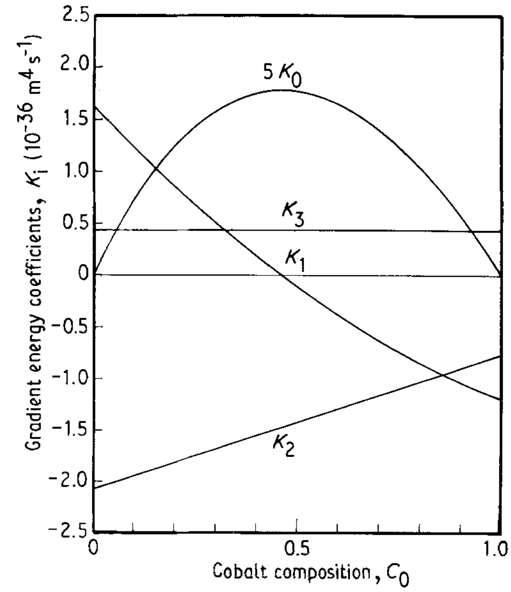

Figure 3 Changes in gradient energy coefficients K_0, K_1, K_2 and K_3 with the average solute composition C_0.

TABLE I The numerical values used for calculation

Temperature, $T(K)$	1173
Average composition, C_0	0.2, 0.5
Binodal compositions, C_{eq1} C_{eq2}	0.03, 0.95
Spinodal compositions, C_{sp1}, C_{sp2}	0.15, 0.79
Mobility of atoms, $M_0(m^4 \cdot J^{-1} \cdot s^{-1})$	4.14×10^{-21}
Reciprocal of calculation region, $\beta(m^{-1})$	5.03×10^7
Interatomic distance, $r_0(m)$	2.56×10^{-10}

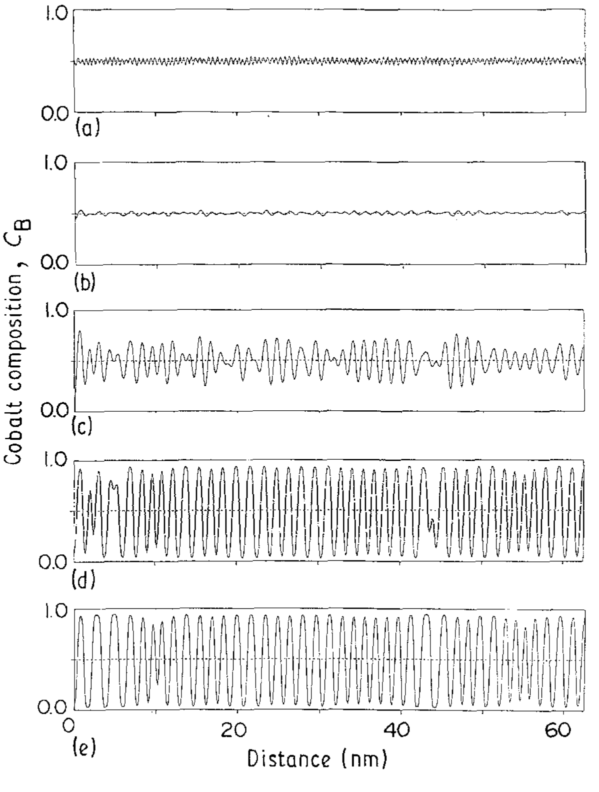

Figure 4 Time development of the composition profiles with progress of ageing at 1173 K for the alloy of symmetric composition ($C_0 = 0.5$). (a) 0 ms, (b) 5.72 ms, (c) 14.3 ms, (d) 28.6 ms, (e) 57.2 ms.

4. Results and discussion

Fig. 4 shows a time evolution of the phase decomposition with ageing time for the case of symmetric composition $C_0 = 0.5$. It is clearly recognized from the figure that the heights of the composition peaks increase with ageing time but stop increasing at the equilibrium composition given by Fig. 1, and then the peaks become rectangular. The details of the composition profiles are shown later in Fig. 6.

Fig. 5 shows the calculation results for the asymmetric alloy of $C_0 = 0.2$. The composition peaks decrease in number and the average peak distance increases in comparison with that of Fig. 4. The heights of some composition peaks increase temporarily but begin to decrease in the course of decomposition such as in the zones marked by the downward pointing arrows in the Figure. Such a competitive growth between the peaks gives rise to microstructure coarsening during phase decomposition.

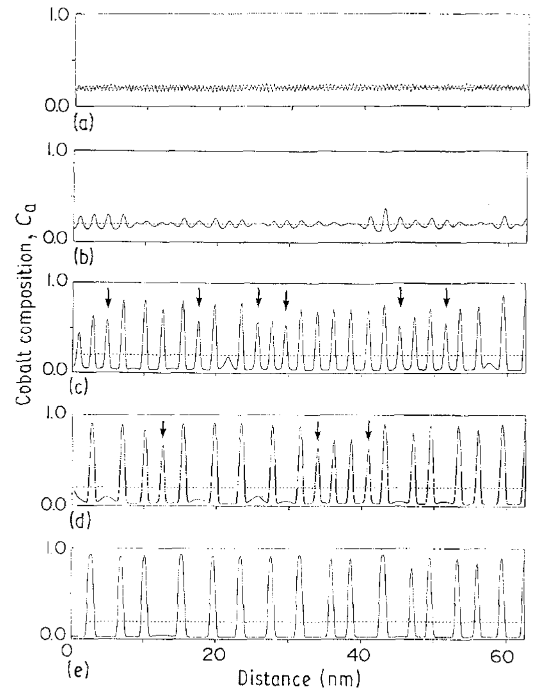

Figure 5 Time development of the composition profiles with progress of ageing at 1173 K for the alloy of asymmetric composition ($C_0 = 0.2$). (a) 0 ms, (b) 57.2 ms, (c) 143.0 ms, (d) 286.0 ms, (e) 572.0 ms.

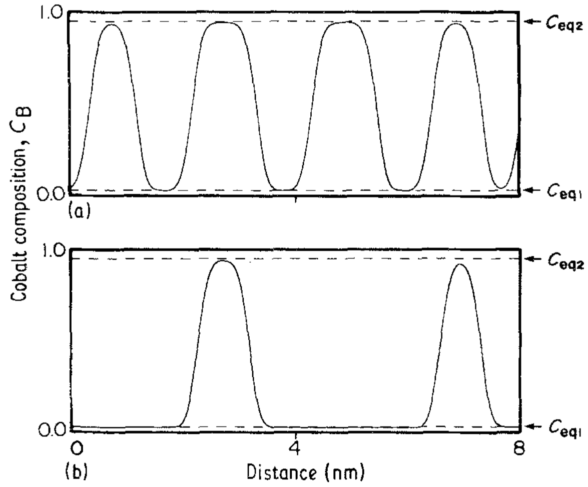

Figure 6 Enlarged composition profiles of the left-hand side region (0–8 nm from the left end) in Figs 4e and 5e. (a) 57.2 ms, $C_0 = 0.5$, (b) 572.0 ms, $C_0 = 0.2$.

Fig. 6a and b show the enlarged composition profiles of Figs 4 and 5, respectively. It is clearly recognized from the Figure that the heights of the composition peaks increase with ageing time but stop increasing exactly at the equilibrium composition C_{eq1} and C_{eq2}, and then the peaks become rectangular.

In a recent paper [15], we proposed a new expression for the non-linear diffusion equation on the basis of the regular solution approximation, and practiced computer simulations of phase decomposition for which we assume the interaction parameter, Ω, between the nearest neighbour atoms, to be independent of composition. In the present, however, we showed the phase decompositions of the actual alloy system, i.e. of Cu–Co alloys, which has an asymmetric interaction parameter with composition. The simulation results performed here obviously show that the new calculation method developed by us is useful for application to the actual alloy systems.

5. Conclusions

Computer simulations of phase decomposition were successfully performed for the Cu–Co alloy system on the basis of the new calculation method recently proposed by us for the non-linear diffusion equation. The calculation method is applicable to many alloy systems whose interaction parameters change with temperature and composition.

Acknowledgements

The authors thank Dr M. Doi and Dr T. Kozakai, Nagoya Institute of Technology, for discussions. This work was financially supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Japan.

References

1. J. E. HILLIARD, in "Phase Transformation", edited by H. I. Aaronson, (ASM. Metals Park, OH, 1970) p. 497.
2. J. W. CAHN and J. E. HILLIARD, *J. Chem. Phys.* **28** (1958) 258.
3. M. HILLERT, *Acta Metall.* **9** (1961) 525.
4. J. W. CAHN, *ibid.* **9** (1961) 795.
5. L. A. SWANGER, P. K. GUPTA and A. R. COOPER Jr, *ibid.* **18** (1970) 9.
6. J. S. LANGER, M. BAR-ON and H. D. MILLER, *Phys. Rev. A* **11** (1975) 1417.
7. T. TSAKALAKOS, *Scripta Metall.* **15** (1981) 255.
8. T. TSUJIMOTO, *Trans. JIM* **21** (1980) 458.
9. *Idem, ibid.* **22** (1981) 127.
10. *Idem, ibid.* **22** (1981) 614.
11. *Idem, ibid.* **23** (1982) 303.
12. T. MIYAZAKI, T. KOZAKAI, S. MIZUNO and M. DOI, *ibid.* **24** (1983) 246.
13. *Idem, ibid.* **24** (1983) 799.
14. T. MIYAZAKI, T. KOZAKAI and T. KOYAMA, to be published.
15. T. MIYAZAKI, A. TAKEUCHI, T. KOYAMA and T. KOZAKAI, submitted to *Mater. Trans., J.I.M.*
16. M. HASEBE and T. NISHIZAWA, *CALPHAD* **4** (1980) 83.

Received 15 January
and accepted 7 June 1991