ESTABLISHMENT AND APPLICATIONS OF MATHEMATICAL MODELS FOR CONCENTRATION DISTRIBUTION IN Mo-Fe-Ni-Co DIFFUSION QUARTERNARY①

(Ⅱ) Characteristics and Applications of Mathematical Models②

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ABSTRACT The characteristics of the mathematical models for concentration distributions such as smoothing property, approximation, tangency, shape preserving property and coordination were analysed, and application examples of the mathematical models were given. The results show that the equilibrium compositions of all components at any point on the two-dimensional plane of the Mo-Fe-Ni-Co diffusion quarternary can be calculated by means of the above mentioned mathematical models, and that the combination of the multi-component diffusion couple technique with the above models can be used to deal with diffusion problems and phase diagram calculation.

Key words concentration diffusions mathematical models phase diagram calculations diffusion

1 INTRODUCTION

Previously, only the concentration variation in one-dimension was considered in general in the study of diffusion problems using the diffusion couple technique. Up till now, no literatures have been reported on the study of the concentration distributions in two dimensions of all components in the multi-component diffusion couple specimens by means of mathemical models for concentration distributions. This paper is aimed at analysing application examples of the mathematical models for concentration distributions in two dimensions of the Mo-Fe-Ni-Co diffusion quarternary based on probing their characteristics.

2 CHARACTERISTICS OF MATHEMATICAL MODELS

Take the concentration distribution function $z = S(x, y)$ expressed by eq. (10) in paper (Ⅰ)[1] as an example to discuss the characteristics of the mathematical models. The following discussion is valid for the other nine models expressed by eqs. (11) ~ (19) in paper(Ⅰ).

2.1 Smoothing property

The smoothing property refers to that the concentration profile $z = S(x, y)$ is a smooth

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curved surface, and this function still changes linearly along the y axis.

In fact, it is known from eq. (9) that the third-order B-type spline function, $M_3(x)$, has continuous first-order derivative, therefore the above conclusion is true according to eq. (10).

2.2 Approximation

The approximation refers to that the following equation holds true for Fig. 4 in paper(Ⅰ):

$$|F(x_i, 20) - \zeta_i| \leqslant \frac{1}{8}|\zeta_{i-1} - 2\zeta_i + \zeta_{i+1}| \quad (i = 1, 2, \cdots, 7)$$

In fact, the combination of Fig. 4 and Eqs. (8) and (9) in paper (Ⅰ) gives

$$\begin{aligned} F(x_i, 20) &= \sum_{k=0}^{8} \zeta_k M_3\left(9 - k + \frac{-180 + 20i}{20}\right) \\ &= \sum_{k=0}^{8} \zeta_k M_3(i - k) \\ &= \zeta_{i-1} M_3(i - i + 1) + \zeta_i M_3(i - i) \\ &\quad + \zeta_{i+1} M_3(i - i - 1) \\ &= M_3(1)(\zeta_{i-1} + \zeta_{i+1}) + M_3(0)\zeta_i \\ &= 0.125(\zeta_{i-1} + \zeta_{i+1}) + 0.75\zeta_i \end{aligned}$$

Therefore

$$|F(x_i, 20) - \zeta_i| \leqslant |0.125(\zeta_{i-1} + \zeta_{i+1}) - 0.25\zeta_i| = \frac{1}{8}|\zeta_{i-1} - 2\zeta_i + \zeta_{i+1}|$$

2.3 Tangency

The tangency refers to that the concentration curve $z = F(x, 20)$ in Fig. 4 of paper(Ⅰ) is tangential to each straight line segment on broken line AB at its middle point, i.e.

$$\begin{cases} F(x_i + 10, 20) = \dfrac{1}{2}(\zeta_i + \zeta_{i+1}) \\ F'_i(x_i + 10, 20) = \zeta_{i+1} - \zeta_i \end{cases} \quad (i = 1, 2, \cdots, 7)$$

According to eq. (9), we get

$$\begin{aligned} &F(x_i + 10, 20) \\ &= \sum_{k=0}^{8} \zeta_k M_3\left(9 - k + \frac{-180 + 20i + 10}{20}\right) \\ &= \sum_{k=0}^{8} \zeta_k M_3(i - k + 0.5) \\ &= \zeta_i M_3(i - i + 0.5) + \\ &\quad \zeta_{i+1} M_3(i - i - 1 + 0.5) \\ &= \frac{1}{2}(\zeta_i + \zeta_{i+1}) \end{aligned}$$

$$F(x, 20) = \sum_{k=0}^{8} \zeta_k M_3\left(9 - k + \frac{x}{20}\right)$$

$$F'_x(x, 20) = \sum_{k=0}^{8} \zeta_k M'_3\left(9 - k + \frac{x}{20}\right)$$

$$\begin{aligned} F'_x(x_i + 10, 20) &= \sum_{k=0}^{8} \zeta_k M'_3 \times \\ &\quad (i - k + 0.5) \\ &= \zeta_i M'_3(0.5) + \\ &\quad \zeta_{i+1} M'_3(-0.5) \\ &= \zeta_{i+1} - \zeta_i \end{aligned}$$

2.4 Shape preserving property

The shape preserving property refers to that the following equation holds true for Fig. 4 in paper(Ⅰ):

$$F''_x(x_i, 20) = \zeta_{i+1} - 2\zeta_i + \zeta_{i-1} \quad (i = 2, 3, \cdots, 6)$$

and the concentration curve $z = F(x, 20)$ passes points A and B.

According to eq. (9), we can obtain

$$\begin{aligned} F''_x(x_i, 20) &= \sum_{k=0}^{8} \zeta_k M''_3\left(9 - k + \frac{-180 + 20i}{20}\right) \\ &= \sum_{k=0}^{8} \zeta_k M''_3(i - k) \\ &= \zeta_{i-1} M''_3(1) + \zeta_i M''_3(0) + \\ &\quad \zeta_{i+1} M''_3(-1) \\ &= \zeta_{i-1} - 2\zeta_i + \zeta_{i+1} \end{aligned}$$

$$\begin{aligned} F(x_1, 20) &= \sum_{k=0}^{8} \zeta_k M_3\left(9 - k + \frac{-160}{20}\right) \\ &= \sum_{k=0}^{8} \zeta_k M_3(1 - k) \\ &= \zeta_0 M_3(1) + \zeta_1 M_3(0) + \\ &\quad \zeta_2 M_3(-1) \\ &= 0.125\zeta_0 + 0.75\zeta_1 + \\ &\quad 0.125\zeta_2 \\ &= 0.125(2\zeta_1 - \zeta_2) + 0.75\zeta_1 + \\ &\quad 0.125\zeta_2 \\ &= \zeta_1 \end{aligned}$$

Similarly, we can obtain $F(x_7, 20) = \zeta_7$. Therefore $z = F(x, 20)$ passes A and B.

2.5 Coordination

The coordination refers to that the three concentration functions for Mo, Ni and Fe, i.e. $M(x, y)$, $N(x, y)$ and $F(x, y)$, expressed by eq. (10) in paper(Ⅰ) satisfy

$$M(x, y) + N(x, y) + F(x, y) \equiv 100$$

In fact, the concentration sum of Mo, Ni

and Fe at point 23′ is 100, and the cases for points 17, 18, …, 23, 40, 41, …, 46 are the same, therefore

$$M(x, y) + N(x, y) + F(x, y) \equiv 100 \sum_{k=0}^{8} M_3(9 - k + \frac{x}{20})$$

as long as the following is proved.

$$\sum_{k=0}^{8} M_3(9 - k + \frac{x}{20}) = 1 \quad (-160 \leqslant x \leqslant 40)$$

Let $x = -180 + 20i + 20t$ ($i = 1, 2, \cdots, 6$; $0 \leqslant t \leqslant 1$), then

$$\begin{aligned}
&\sum_{k=0}^{8} M_3(9 - k + \frac{x}{20}) \\
&= \sum_{k=0}^{8} M_3(i - k + t) \\
&= \sum_{k=i-1}^{i+2} M_3(i - k + t) \\
&= M_3(1 + t) + M_3(t) + M_3(t - 1) + M_3(t - 2) \\
&= \begin{cases}
[\frac{(t+1)^2}{2} - \frac{3}{2}(t+1) + \frac{9}{8}] + [\frac{3}{4} - t^2] + [\frac{(t-1)^2}{2} - \frac{1}{2}(1-t) + \frac{9}{8}] = 1 \\
\quad (0 \leq t < \frac{1}{2};\ i = 1, 2, \cdots, 6) \\
[\frac{t^2}{2} - \frac{3}{2}t + \frac{9}{8}] + [\frac{3}{4} - (t-1)^2] + [\frac{(t-2)^2}{2} - \frac{3}{2}(2-t) + \frac{9}{8}] = 1 \\
\quad (\frac{1}{2} \leqslant t \leqslant 1;\ i = 1, 2, \cdots, 6)
\end{cases}
\end{aligned}$$

3 CALCULATION EXAMPLES

Take the calculation of the concentration of one component at any point (x, y) in the δ MoNi phase region in paper(Ⅰ) as an example. Because

$$M_3(x) = 0, \quad (|x| \geqslant 1.5)$$

for any point (x, y) in the δ MoNi region, there are at the most three nonzero terms on the right side of eq. (10). For instance, in order to calculate the concentration of Fe at point $(-80, 20)$, $z = F(-80, 20)$, it is necessary to calculate the value of $M_3(k + \frac{x}{20})$ in eq. (1) first:

$$\begin{aligned}
M_3(k + \frac{-80}{20}) &= M_3(k - 4) \\
&= \begin{cases}
0 & (k = 1, 2, 6, 7, 8, 9) \\
1/8 & (k = 3) \\
3/4 & (k = 4) \\
1/8 & (k = 5)
\end{cases}
\end{aligned}$$

Thus

$$\begin{aligned}
z &= F(-80, 20) \\
&= [z_{20} + \frac{z_{43} - z_{20}}{31} \times 17] \times \frac{1}{8} + [z_{21} + \frac{z_{44} - z_{21}}{34} \times 16] \times \frac{3}{4} + [z_{22} + \frac{z_{45} - z_{22}}{29} \times 12] \times \frac{1}{8}
\end{aligned}$$

Substituting the concentrations of Fe of related points into the above equation gives $z = F(-80, 20) = 8.71$. Therefore, the concentration of Fe at point $(-80, 20)$ is 8.71% in mole. Take point 74(11, 40) in the *bcc* (Mo) region of Fig. 1 in paper(Ⅰ) as another example. The concentration of Fe at this point determined by electron probe microanlysis is 2.37. The concentrations at this point have not found use in Eq. (14) of paper(Ⅰ), therefore let′s calculate the concentration of Fe by means of model (14) as follows:

$$\begin{aligned}
z &= F(11, 40) \\
&= [0.72 + \frac{0.37 - 0.72}{148}(40 - 32)] \times M_3(1.275) + [1.96 + \frac{0.99 - 1.96}{144} \times (40 - 36)] M_3(0.275) + [3.18 + \frac{1.79 - 3.18}{116}(40 - 64)] M_3(0.725) \\
&= 0.017\,746\,1 + 1.303\,604\,4 + 1.041\,359\,5 \\
&= 2.362\,71
\end{aligned}$$

The absolute and relative errors between this calculated value and the above experimental value are 0.007 29 and 0.3%, respectively. Therefore the precision of the model is satisfying.

According to the discussion concerning the characteristics of the mathematical models and the calculation examples, a conclusion can be drawn that the mathematical models for concentration distributions on the two-dimensional plane of the Mo-Fe-Ni-Co diffusion quarternary have the following characteristics.

(1) The concentrations of Mo, Fe, Ni and

Co at any point on the two-dimensional plane of the diffusion quarternary can be calculated by means of the limited experimental concentration data in combination with the mathematical models.

(2) Their function expressions are the simplest polynominals which are easy to calculate.

(3) The calculations are precise and reliable.

(4) Their smoothing property, integral approximation, tangency, shape preserving property and coordination are excellent.

4 APPLICATION EXAMPLES OF MATHEMATICAL MODELS

4.1 Application to treatment of diffusion problems

Fick's second law of diffusion can be used to deal with unsteady-state diffusion problems. The solution of Fick's equation depends on the geometric shape of the specimens, the initial and boundary conditions of the concentrations of the specimens. Therefore, the calculation is relatively complicated[2].

A Mo-Fe-Ni-Co diffusion quarternary was prepared by the authors. After annealing at 1 200 ℃ for 400 h, limited experimental data of the concentration of this diffusion quarternary were determined using electron probe microanalysis[3, 4]. The concentrations $z\,(z = F(x, y))$ at any point in the diffusion quarternary can be calculated rapidly by means of those experimental data in combination with the mathematical models established. Thus, the concentration profile of each component can be described audio-visually in the three-dimensional space. For example, the concentration profile of Fe in the Mo-Ni-Fe ternary system, as shown in Fig. 1, was drawn by means of models(10) ~ (15) in paper (Ⅰ); the concentration profile of Mo in the Mo-Ni-Co ternary system, as shown in Fig. 2, was drawn by means of models(16) ~ (19). Obviously, it is convenient and audio-visual to describe the diffusion problems under concentration gradient with the mathematical models established by the authors.

4.2 Application to phase diagram calculation

The determination of phase diagrams by

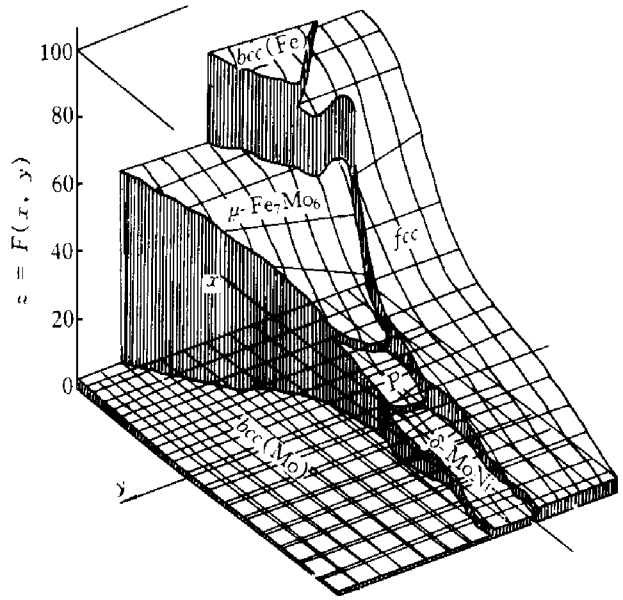

Fig. 1 Concentration profile of Fe in Mo-Fe-Ni ternary system

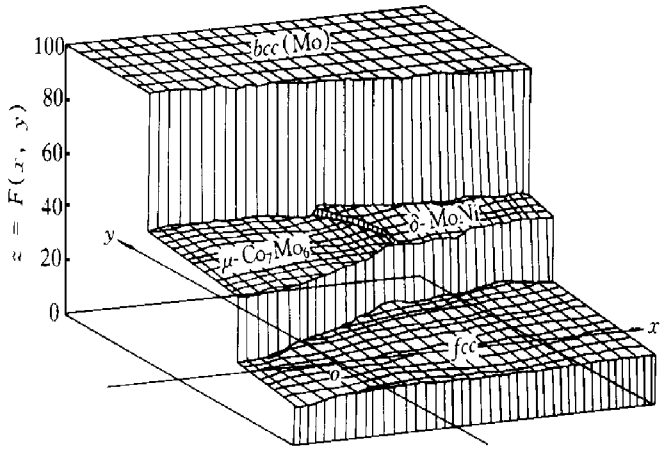

Fig. 2 Concentration profile of Mo in Mo-Ni-Co ternary system

means of diffusion couple technique is based on the local equilibria principle between phase boundaries, which are established after annealing at a certain temperature. A series of tie-lines can be obtained by determing the equilibrium compositions of two phases in phase interface using electron probe microanalysis. Similarly, several tie-triangles can be obtained at the intersection interface of three phases in ternary systems. By means of the phase-contact rules, an isothermal

section at a certain temperature for a ternary system can be built up on the basis of the phase region distributions and the determined equilibrium compositions[3, 4].

The establishment of the mathematical models for concentration distributions in the Mo-Ni-Fe-Co diffusion quarternary will help to calculate the two ternary isothermal sections included in the diffusion quarternary. For example, as mentioned above, the concentration of Fe at point 74(11, 40) on the *bcc* (Mo) side at the three phases intersection interface of *bcc* (Mo), *P* and μ Fe_7Mo_6 in the Mo-Fe-Ni ternary system[1] was obtained:

$$z = F(11, 4) = 2.36271$$

Similarly, the concentrations of Mo and Ni at point 74(11, 40) were calculated, thus the equilibrium compositions of *bcc* (Mo) phase in the equilibrium tie-triangle was obtained. The equilibrium compositions of *P* phase and μ Fe_7Mo_6 phase were calculated by means of models (11) and (12) at the three phases intersection interface, respectively. Therefore the three phases equilbrium compositions of three phases region (*bcc* (Mo) + *P* + μ Fe_7Mo_6) were known. Similarly, in the diffusion quarternary, the two phases equilibrium compositions of any equilibium tie-line at the phase boundary could be calculated. Synthesizing all the phase equilibium data obtained, we can obtain a complete ternary isothermal section. Thus it can be seen that by means of the mathematical models for concentration distributions in the Mo-Fe-Ni-Co diffusion quarternary the concentration at any point (x, y) on the phase boundaries in the Mo-Fe-Ni or Mo-Ni-Co ternary systems can be calculated directly. Using the concentration data calculated, a series of tie-lines and tie-triangles can be drawn, consequently the two ternary isothermal sections at 1200 ℃ in the Mo-Fe-Ni-Co diffusion quarternary can be constructed.

5 CONCLUSIONS

The two-dimensional mathematical models for concentration distributions in the Mo-Fe-Ni-Co diffusion quarternary, which were established by means of B-type spline functions, are characterized by good smoothness, integral approximation, tangency, shape preserving property, coordination and simiplicity and precision in calculation. The equilibrium composition at any point in the two-dimensional plane of the specimen can be calculated with those mathematical models. Therefore, the combination of the multi-component diffusion couple technique with the concentration distributions mathematical models can be used to deal with diffusion problems and phase diagram calculations.

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