JOURNAL OF MATERIALS SCIENCE 21 (1986) 2283–2288

An analytical method of calculating variable diffusion coefficients

N. SARAFIANOS
Department of Mechanical Engineering, Laboratory of Physical Metallurgy, School of Engineering, University of Thessaloniki, Thessaloniki, Greece

An analytical method of calculating variable diffusion coefficients has been developed. The Boltzmann–Matano graphical method used up to now has certain disadvantages which restrict the acuracy of the evaluated diffusion coefficients. Due to these disadvantages, the accuracy of this method is restricted even more when diffusion coefficients are determined in an area of low concentration of the diffused species of atom. The reliability of the analytical expression obtained in the present investigation has been verified experimentally by comparing the results obtained with those of the graphical method. On the basis of this comparison the analytical method can claim an accuracy better than, or at least equal to, that of the graphical method.

1. Introduction

The volume diffusion coefficient (D) of a diffusion process can be determined by solution of the second Fick's law

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \qquad (1)$$

where C is the concentration of the diffused species of atom at distance x. Grube and Jedele [1] obtained the solution of Equation 1 when the diffusion coefficient is independent of the concentration. When the diffusivity is a function of the concentration, the solution of Equation 1 can be expressed [2] as

$$D = -\frac{1}{2}\frac{\mathrm{d}\lambda}{\mathrm{d}C}\int_0^C \lambda \mathrm{d}C \qquad (2)$$

with the variable λ suggested by Boltzmann [3] to be

$$\lambda = x/t^{1/2} \qquad (3)$$

The calculation of D from Equation 2 requires the determination of the integral, which is evaluated graphically [2]. However, errors are introduced in the evaluation of D from Equation 2 for two main reasons: firstly, due to the uncertainty of the Matano interface position the integral in Equation 2 cannot be evaluated correctly, and secondly the value of the slope $\mathrm{d}\lambda/\mathrm{d}C$ is difficult to define accurately, particularly at the two concentration extremes.

Considering the experimental results for diffusion coefficients of da Silva and Mehl [4], as well as the disagreement between theory and chemical diffusion data pointed out by Zener [5] and Nowick [6], Hall [7] derived an analytical expression to evaluate D as a function of concentration. He used the following relationships:

$$\frac{C}{C_0} = \tfrac{1}{2}(1 + \operatorname{erf} u) \qquad (4a)$$

$$\operatorname{erfc} u = \tfrac{1}{2}(1 + \operatorname{erf} u) \qquad (4b)$$

$$u = h\lambda + k \qquad (4c)$$

where C_0 is the initial concentration and h and k are constant parameters. He plotted the concentration against distance as u against λ on semi-probability paper and obtained the formula

$$D = \frac{1}{4h^2} + \frac{k\pi^{1/2}}{2h^2}\exp(u^2)\operatorname{erfc} u \qquad (5)$$

Grank [8] has slightly modified Hall's expression by using the Boltzmann variable λ divided by two. He also avoided using the error function of Equation 4b because it is not in standard notation [9], and obtained the formula

$$D = \frac{1}{h^2} + \frac{k\pi^{1/2}}{h^2}(1 + \operatorname{erf} u)\exp(u^2) \qquad (6)$$

In the present investigation the analytical method developed by Hall [7] has been modified and extended at intermediate concentrations in order to establish an analytical expression determining variable diffusion coefficients over the whole concentration range. Finally, the results of the analytical method and the Boltzmann–Matano graphical method are compared.

2. Theoretical considerations

From the above section it is clear that the plot of concentration against distance on a semi-probability paper (Fig. 1) yields a curve with straight-line parts in the regions of low and high concentrations. Thus, the slope and the intersection with the vertical axis ($x = 0$) of these two straight lines can be evaluated as the constants h and k, respectively. Furthermore, using these constants through the following set of relationships [1, 9]

$$\frac{C}{C_\infty} = \tfrac{1}{2}\operatorname{erfc} u \qquad (7a)$$

$$\operatorname{erfc} u = 1 - \operatorname{erf} u \qquad (7b)$$

$$u = hx + k \qquad (7c)$$

$$\operatorname{erf} u = \frac{2}{\pi^{1/2}}\int_0^u \exp(-z^2)\,\mathrm{d}z \qquad (7d)$$

0022–2461/86 $03.00 + .12 © *1986 Chapman and Hall Ltd.*

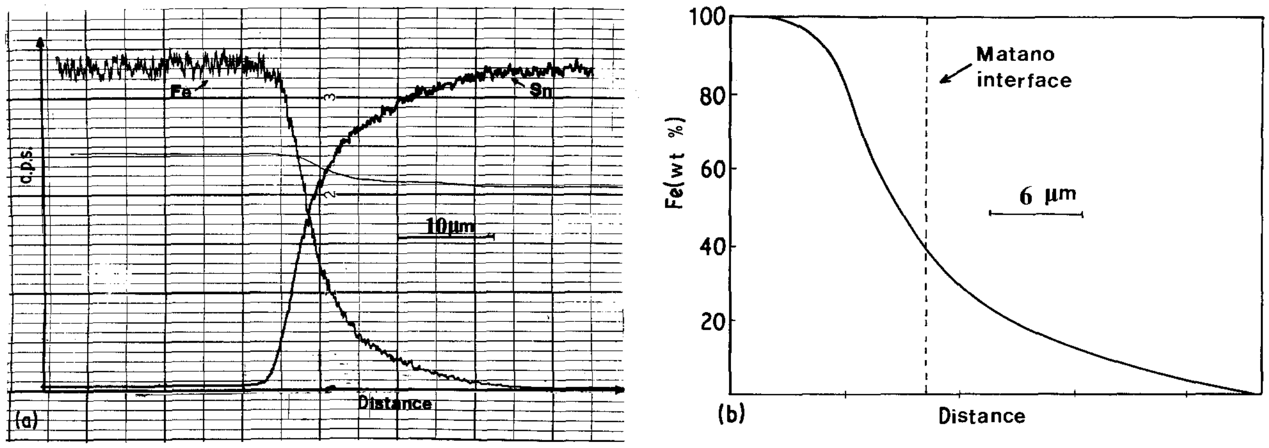

Figure 1 (a) Diffusion profile and (b) concentration against distance across the interface of Fe–50% Sn diffusion sample, 200° C.

and taking the Boltzmann parameter λ equal to

$$\lambda = x/2t^{1/2} \tag{8}$$

Equation 1 results in

$$-\frac{x}{2t}\mathrm{d}C = d\left(D\frac{\mathrm{d}C}{\mathrm{d}x}\right) \tag{9a}$$

For the solution of Equation 9a we distinguish the three cases discussed below.

2.1. Low-concentration region

In this case we consider the following boundary conditions:

for $x \to \infty$ then $C \to 0$ and $\mathrm{d}C/\mathrm{d}x \to 0$

for $x \to x_m$ then $C \to C_\mathrm{m}$

and $\mathrm{d}C/\mathrm{d}x \to$ to a certain value

where x_m is the position of Matano interface. According to these boundary conditions, integration of Equation 9a gives

$$-\frac{1}{2t}\int_C^0 x\mathrm{d}C = -D\frac{\mathrm{d}C}{\mathrm{d}x} \tag{9b}$$

Differentiating Equation 7a and substituting into Equation 9b D is evaluated as

$$D = \frac{1}{2t}\exp(u^2)\int_x^\infty x\exp(-u^2)\mathrm{d}x \tag{10a}$$

The calculation of the integral in Equation 10a (see Appendix) gives

$$D = \frac{1}{4h^2t}(1 - k\pi^{1/2}\exp(u^2)\operatorname{erfc} u) \tag{10b}$$

2.2. High-concentration region

The boundary conditions in this case are

for $x \to -\infty$ then $C \to C_\infty$ and $\mathrm{d}C/\mathrm{d}x \to 0$

for $x \to x_\mathrm{m}$ then $C \to C_\mathrm{m}$

and $\mathrm{d}C/\mathrm{d}x \to$ to a certain value

Integration of Equation 9a with the new boundary conditions results in

$$-\frac{1}{2t}\int_0^C x\mathrm{d}C = D\left(\frac{\mathrm{d}C}{\mathrm{d}x}\right) \tag{11}$$

Again, differentiating Equation 7a and substituting into Equation 11, D is obtained as

$$D = -\frac{1}{2t}\exp(u^2)\int_{-\infty}^x x\exp(-u^2)\,\mathrm{d}x \tag{12a}$$

Evaluation of the integral in Equation 12 (see Appendix) gives

$$D = \frac{1}{4h^2t}(1 - k\pi^{1/2}\exp(u^2)\operatorname{erfc} u) \tag{12b}$$

2.3. Intermediate range of concentration

At intermediate compositions the variation of the concentration as a function of the penetration depth (Fig. 2) is not linear [7]. This means that the parameters h, k which are constant in the regions of low and high concentrations, in the intermediate concentration range are varying with distance. Therefore

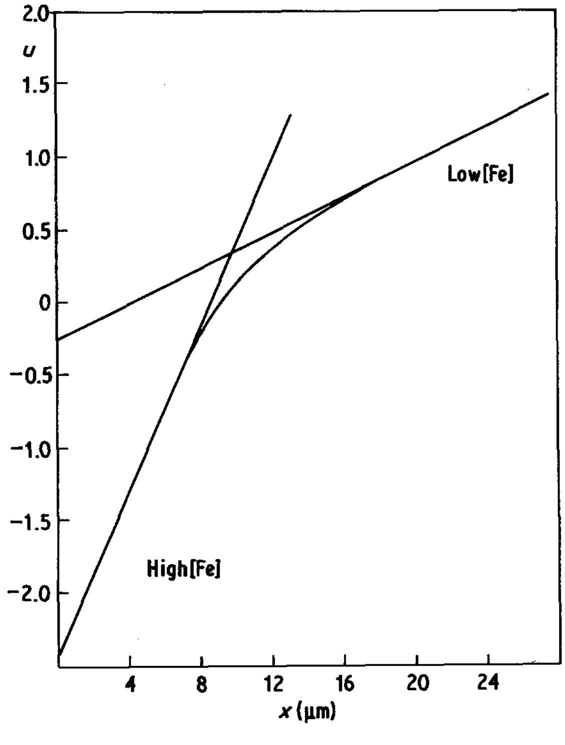

Figure 2 Semi-probability plot of concentration distribution against distance for the Fe–50% Sn sample. At high iron concentration h_A = 2650. k_A = −2.30535; at low concentration h_B = 605.5, k_B = − 0.25358.

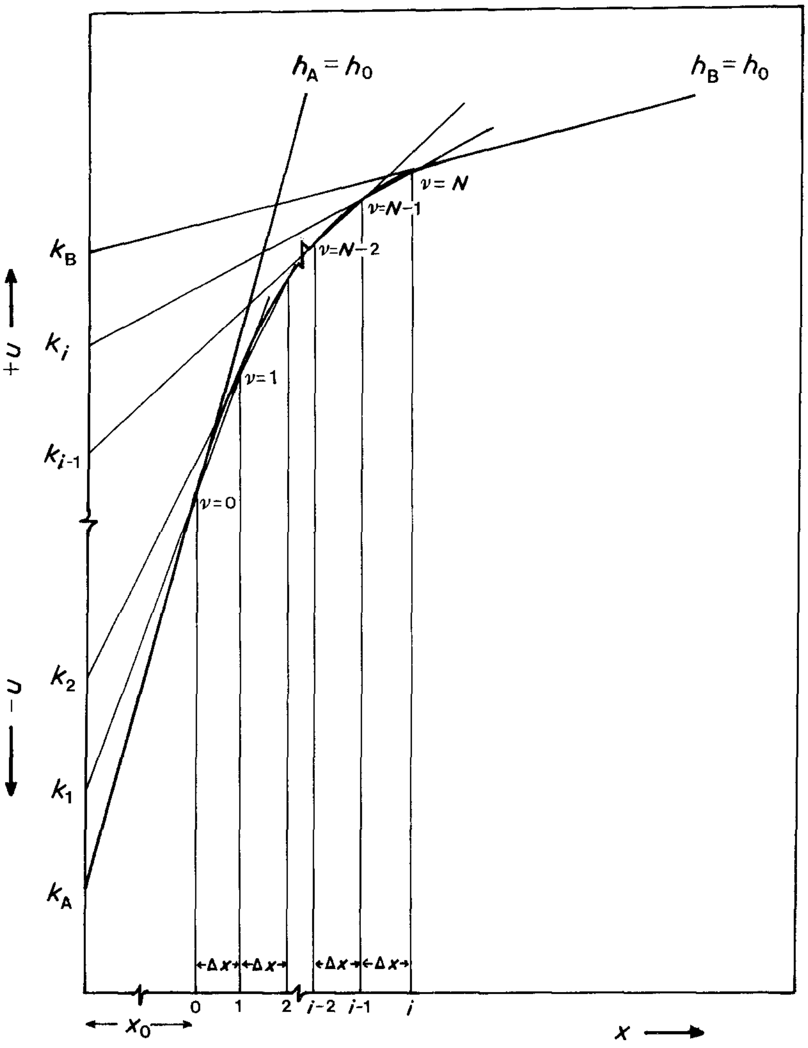

Figure 3 Semi-probability plot of a diffusion profile dependent on concentration.

Equations 10b and 12b can be applied in the intermediate concentration region if the h_i, k_i at each point can be determined. Determination of these parameters has been worked out by an arithmetical method based on the geometrical meaning of the derivative [10] in the following way.

Firstly, let the curved part of the plot in Fig. 2 be dividied into N elementary sections (Figs. 3 and 4), and secondly consider the tangent of each section which is drawn parallel to the corresponding chord on each elementary bow section. The tangent touches each bow almost in the middle, and hence the pair h_i, k_i are determined from the slope and the intersection with the vertical axis, respectively. The variation of the tangent between two successive sections determines the slope change and can be calculated according to the trigonometrical relationship

$$\tan \omega_i = \tan(\omega_{i-1} - \Delta\omega_i) \qquad (13)$$

where ω_i is the angle between the horizontal axis and the tangent at the corresponding bow (Fig. 3). The development of Equation 13 gives

$$\tan \omega_i = \frac{\tan \omega_i - \tan(\Delta\omega_i)}{1 + \tan \omega_i \tan(\Delta\omega_i)} \qquad (14a)$$

For sufficiently large value of N, two approximations are introduced without significant errors: firstly, the variation in the slope of the tangent between two successive sections is so small that we can consider $\tan \Delta\omega_i \to 0$. Equation 14a is then simplified to

$$\tan \omega_i = \tan \omega_{i-1} - \tan \Delta\omega_i \qquad (14b)$$

which is equivalent to

$$h_i x_i = h_{i-1} x_i - \Delta h_i x_i \qquad (14c)$$

and finally results in

$$h_i = h_{i-1} - \Delta h_i \qquad (15)$$

Secondly, the variance in the intercept to the tangent with the vertical axis in two successive sections Δk can be taken equal from section to section and can be expressed by

$$\Delta k = \frac{k_A - k_B}{N} = k_A - k_1 = k_1 - k_2 = \dots$$
$$= k_{i-1} - k_i = k_i - k_B \qquad (16)$$

The above approximations give the possibility of describing any intermediate concentration accurately by a linear function. Each concentration can be considered as the intersection point between the elementary bow and the corresponding chord (Fig. 3). This point can now easily be described by the following pair of the linear equations:

$$\text{for } \nu = 0 \quad u_0 = h_0 x_A + k_0$$
$$u_0 = h_1 x_A + k_1 \qquad (17a)$$

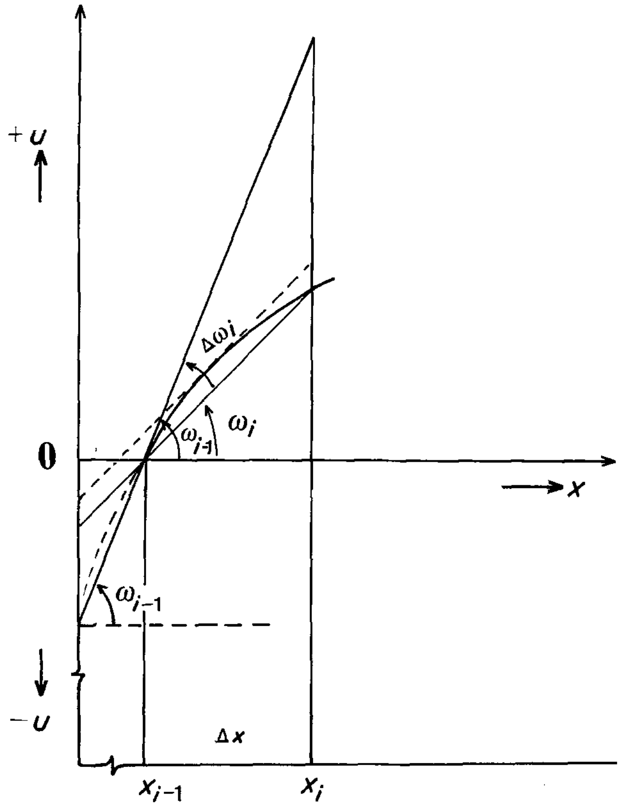

Figure 4 Magnified elementary section of Fig. 3 at intermediate concentration, showing the variation of the angle ω between the horizontal axis and the tangent.

$$\text{for } v = 1 \quad u_1 = h_1(x_A + \Delta x) + k_1$$
$$u_0 = h_2(x_A + \Delta x) + k_2 \qquad (17b)$$

or generally

$$\text{for } v = i - 1 \quad u_{i-1} = h_{i-1}[x_A + (i-1)\Delta x] + k_{i-1}$$
$$u_{i-1} = h_i\,[x_A + (i-1)\Delta x] + k_i \qquad (17c)$$

with the boundary conditions

$$\text{for } v = 0 \qquad h_0 = h_A,\ k_0 = k_A$$
$$\text{for } v = N \qquad h_N = h_B,\ k_N = k_B \qquad (17d)$$

From the two equations of general form (Equations 17c) the variation in the parameter h for two successive sections can be obtained by subtraction as

$$\Delta h_i = h_{i-1} - h_i = \frac{k_i - k_{i-1}}{x_A + (i-1)\Delta x} \qquad (18)$$

Finally, any intermediate concentration can be expressed by the linear function

$$u_{i-\frac{1}{2}} = h_i\,[x_A + (i - \tfrac{1}{2})\Delta x] + k_i \qquad (19)$$

which determines the midpoint of each elementary bow section in which the tangent is drawn.

From Equations 10b and 12b the diffusion coefficients can be calculated for any concentration C_i because Equation 19 defines the function u at any distance. The parameter h_i can be calculated from Equation 15 provided that the difference Δh_i is known. This difference is calculated from Equation 18 using Equation 16. Finally, the parameter k_i can be calculated from Equation 16 with the help of the boundary conditions (Equations 17d), and therefore the function u can be evaluated.

3. Experimental application and discussion

The accuracy of the analytical method developed to calculate variable diffusion coefficients has been verified experimentally. For this purpose, two series of diffusion data coming from independent sources of diffusion processes have been checked. Bearing in mind that diffusion couples should clearly express the dependence of diffusion on concentration [11], convenient binary systems of Fe/50% Sn and Fe/Fe–24.2 at % Ni [12] where chosen to satisfy this condition. However, the study of the diffusion process was restricted to the first system only, and the diffusion couple was prepared in the following way.

A small disc of 0.25 mm thickness was cut off from a commercial coil of mild steel specified by ASTM 623. After careful cleaning of the surface in 10% NaOH solution and pickling in 10% Na_2CO_3 solution, the disc was tin-electroplated for a convenient time to get a tin layer of about 0.25 mm thickness at 20° C. Pure tin specified by ASTM 339 was used as the anode in a solution for the "halogen" process of tin-plating. In the next stage the diffusion couple obtained was put into the furnace and annealed for 23 h and 40 min at 200° C, during which the temperature was kept constant within ± 1° C. After quenching in water at 25° C, the sample was cut parallel to the diffusion gradient away from the free interface of iron and tin in order to avoid possible oxidation problems. The sample was then fixed in polyester and polished using diamond paste of 0.25 μm.

The diffusion process was then investigated by means of point-scanning spectroscopy. The microprobe analyser Microscan-5 of the Cambridge Instrument Co. was used to obtain the diffusion profile (Fig. 1a). In order to convert the observed X-ray intensity ratio between specimen and standard to weight concentration the most widely used ZAF correction procedure [13] was applied. The diffusion coefficients

TABLE I Diffusion coefficients in the Fe–Sn system calculated by different methods

Distance (μm)	Concentration range of iron	D (cm^2 sec^{-1})	
		Boltzmann–Matano method	Present method
4	High	4.36×10^{-13}	7.16×10^{-13}
5	High	4.31×10^{-13}	7.67×10^{-13}
6	High	1.75×10^{-12}	8.35×10^{-13}
7	High	1.18×10^{-12}	9.70×10^{-13}
8		1.23×10^{-12}	1.01×10^{-12}
10	Medium	3.94×10^{-12}	2.95×10^{-12}
12	Medium	5.65×10^{-12}	4.23×10^{-12}
14	Medium	6.01×10^{-12}	7.10×10^{-12}
16	Medium	8.03×10^{-12}	1.25×10^{-11}
18	Low	9.93×10^{-12}	1.42×10^{-11}
28	Low	1.03×10^{-11}	1.60×10^{-11}
22	Low	9.44×10^{-12}	1.84×10^{-11}
24	Low	7.65×10^{-12}	2.16×10^{-11}

were determined first by the Boltzmann–Matano graphical method (Table I) and then by the present analytical method (Fig. 1b and Table II). The values of D obtained by the two methods are found to be in very good agreement.

It is widely believed that the reliability of an analytical method in calculating variable diffusion coefficients can best be verified by analysing the diffusion profiles of other investigators and then comparing the results. Thus, the diffusion profile from the couple Fe/Fe–24.2 at % Ni (Fig. 5) obtained by Goldstein *et al.* [12] was analysed by this method. The atomic percentage of nickel was converted into concentration against distance and then replotted on semi-probability paper (Fig. 6). The values of D along the diffusion zone were calculated analytically. Goldstein *et al.* [12] analysed the same diffusion profile by the graphical method and established the following relationship to calculate D as function of the concentration:

$$D = \exp(0.0515C_{\mathrm{Ni}} + 1.15) \times \exp\left(-\frac{76.000 - 11.6C_{\mathrm{Ni}}}{RT}\right)$$

where C_{Ni} is the atomic percentage of nickel. Table II shows the values of D from both methods, and it is clear that there is very good agreement.

From Equations 10b and 12b it is evident that the evaluated formulae for D at the concentration extremes are identical. Having determined the parameters h, k at both concentration extremes as well as in the intermediate concentration region, it is possible for the value of D to be determined in the whole range of concentration. However, the reliability of the analytical method depends on the accuracy with which the parameters h, k can be evaluated, and two points should be stressed here:

TABLE II Diffusion coefficients from the Fe/Fe–24.2 at % Ni diffusion couple, evaluated by different methods (annealed 4.27 × 10^4 sec at 1288° C)

Distance (μm)	Concentration of nickel		D (cm^2 sec^{-1})	
	at %	wt %	Boltzmann–Matano method	Present method
0	24.2	23.26		
25	23.7	22.75	2.78×10^{-10}	2.87×10^{-10}
50	22.1	21.23	2.55×10^{-10}	2.66×10^{-10}
75	19.25	18.46	2.17×10^{-10}	2.60×10^{-10}
100	13.5	12.93	1.58×10^{-10}	2.35×10^{-10}
125	6.77	6.45	1.09×10^{-10}	1.43×10^{-10}
150	1.3	1.2	8×10^{-11}	1.23×20^{-10}

1. The determination of the parameters h, k at the two concentration extremes as the slope and the intersection of the straight lines is very accurate, because the calculation is always referred to semi-probability paper which is naturally of standard dimensions. The error involved is therefore kept to a minimum.
2. The determination of the parameters h_i, k_i in the curved portion of the concentration curve is dependent on the number of elementary sections taken.

Of course, there is always the possibility of splitting the curve into a sufficiently large number of sections in order to improve the accuracy of the calculation. As N approaches a large number, each elementary bow section and the corresponding chord are coincident and therefore the slope of the tangent in the middle of the bow (Equation 19) as well as the intersection with the vertical axis are determined accurately. Hence the accuracy of the analytical method depends on the accuracy of the parameters h, k determined at the concentration extremes.

On the other hand, the accuracy of the Matano method is restricted by the following errors:

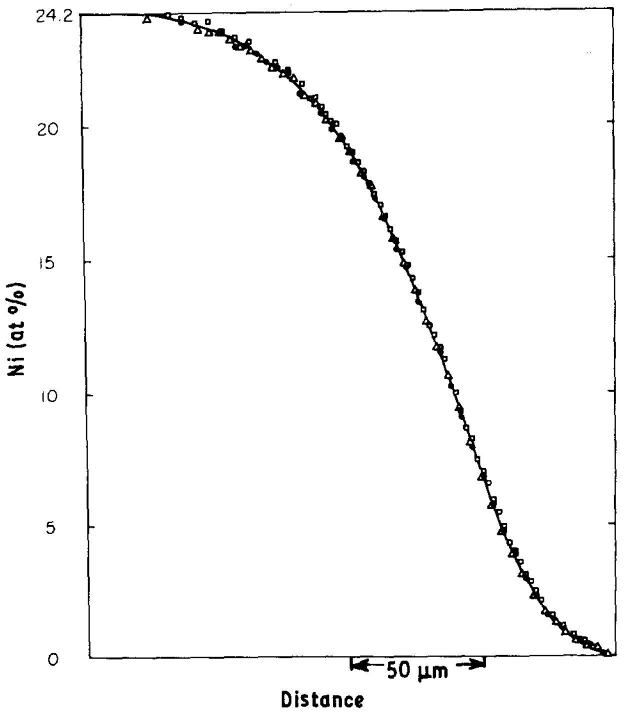

Figure 5 Diffusion profile in the Fe–Ni system (after Goldstein *et al.* [12]). Symbols refer to three different scans.

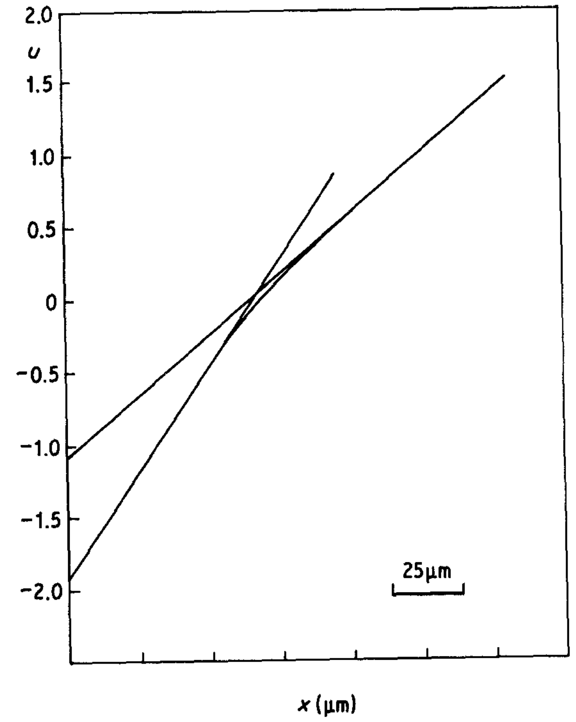

Figure 6 Semi-probability plot of concentration distribution against distance for the Fe/Fe–24.2 at % Ni sample. $h_A = 299$, $k_A = -1.98728$; $h_B = 196.1$, $k_B = 1.27464$.

1. The uncertainty of the Matano interface position restricts the accuracy of the calculated value of the integral $\int_0^C \lambda \, \mathrm{d}C$.
2. The error in the accuracy of the slope $\mathrm{d}\lambda/\mathrm{d}C$ depends on the smoothness of the diffusion curve, and varies for different profiles because their dimensions are only occasionally the same.
3. Determination of the slope $\mathrm{d}\lambda/\mathrm{d}C$ in the profile of a short diffusion zone results in a large error. The same error also applies when D values are evaluated either for high or low concentrations.

Finally, comparison of the accuracy of the two methods depends on the errors involved. Taking into account the errors mentioned above, the analytical method can claim a better accuracy than the graphical one, particularly at the concentration extremes, and therefore the accuracy over the whole concentration range is better.

4. Conclusions

An analytical relationship has been established to give interdiffusion coefficients (D) in the whole concentration range of a binary system.

Comparison between values of D from the analytical and graphical method, show very good agreement. The discrepancy observed in the values of D by the two methods is mainly due to errors involved in the graphical method, and these deteriorate at the concentration extremes.

Appendix

The solution of Equation 1 only exists with the assumption

$$\int_{C=0}^{C=100} x \mathrm{d}C = 0 \qquad \text{(A1)}$$

for the boundary conditions to be satisfied. Putting arbitrarily the Matano Interface at plane $x_\mathrm{M} = x$ the above integral can be split into

$$\int_{C_0}^{C_\mathrm{m}} x \mathrm{d}C + \int_{C_\mathrm{M}}^{C_\infty} x \mathrm{d}C = 0 \qquad \text{(A2)}$$

Differentiation of the Relation 7a and substitution into Equation A2 results in

$$-\frac{C_\infty h}{\pi^{1/2}} \int_{-\infty}^{x} \exp(-u^2)\, x \mathrm{d}x - \frac{C_0 h}{\pi^{1/2}} \times \int_{x}^{\infty} \exp(-u^2)\, x \mathrm{d}x = 0 \qquad \text{(A3)}$$

The calculation of the two integrals in Equation A3 gives

$$\begin{aligned}
\int_{-\infty}^{x} \exp(-u^2)\, x \mathrm{d}x &= \frac{1}{2h^2} \int_{-\infty}^{x} \exp(-u^2)\, \mathrm{d}(hx+k)^2 - \frac{k}{h^2} \int_{-\infty}^{x} \exp(-u^2)\, \mathrm{d}(hx+k) \\
&= \frac{1}{2h^2} \exp(-u^2) - \frac{k\pi^{1/2}}{2h^2} \frac{2}{\pi^{1/2}} \int_{-\infty}^{-x} \exp(-u^2)\, \mathrm{d}u \\
&= -\frac{1}{2h^2} \exp(-u^2) + \frac{k\pi^{1/2}}{2h^2} - \frac{k\pi^{1/2}}{2h^2} \operatorname{erf}(u) \\
&= -\frac{1}{2h^2} \exp(-u^2) + \frac{k\pi^{1/2}}{2h^2} \operatorname{erfc} u \qquad \text{(A4)}
\end{aligned}$$

and

$$\begin{aligned}
\int_{x}^{\infty} \exp(-u^2)\, x \mathrm{d}x &= \frac{1}{2h^2} \int_{x}^{\infty} \exp(-u^2)\, \mathrm{d}(hx+k) - \frac{k}{h^2} \int_{x}^{\infty} \exp(-u^2)\, \mathrm{d}(hx+k) \\
&= \frac{1}{2h^2} \exp(-u^2) - \frac{k\pi^{1/2}}{2h^2} \frac{2}{\pi^{1/2}} \int_{x}^{\infty} \exp(-u^2)\, \mathrm{d}(hx+k) \\
&= \frac{1}{2h^2} \exp(-u^2) - \frac{k\pi^{1/2}}{2h^2} + \frac{k\pi^{1/2}}{2h^2} \operatorname{erf}(u) \\
&= \frac{1}{2h^2} \exp(-u^2) - \frac{k\pi^{1/2}}{2h^2} \operatorname{erfc} u \qquad \text{(A5)}
\end{aligned}$$

References

1. G. GRUBE and A. JEDELE, *Z. Electrochem.* **38** (1932) 799.
2. C. MATANO, *Jpn. J. Phys.* **8** (1983) 109.
3. L. BOLTZMANN, *Ann. Physik* **53** (1894) 959.
4. L. L. C. da SILVA and R. F. MEHL, *J. Metall.* **3** (1951) 155.
5. C. ZENER, *J. Appl. Phys.* **22** (1951) 372.
6. A. S. NOWICK, *ibid.* **22** (1951) 1182.
7. L. D. HALL, *J. Chem. Phys.* **21** (1953) 87.
8. J. CRANK, "The Mathematics of Diffusion" (Oxford University Press, London, 1979) p. 230.
9. H. S. CARSLAW and J. C. JAEGER, "Conduction of Heat in Solids" (Oxford University Press, London, 1959) p. 482.
10. F. SCHEID, "Numerical Analysis" (McGraw-Hill, New York, 1968) p. 100.
11. N. SARAFIANOS, MSc thesis, Sheffield University (1981).
12. J. I. GOLDSTEIN, R. E. HANNEMAN and R. E. OGILVIE, *Trans. Met. Soc. AIME* **223** (1965) 812.
13. C. N. HAWORTH, "Correction Procedure in Electron Probe Microanalysis" (Department of Metallurgy, Sheffield University, 1973).

Received 19 March
and accepted 11 September 1985