Available online at www.sciencedirect.com

ScienceDirect

Computer Coupling of Phase Diagrams and Thermochemistry 32 (2008) 94–100

www.elsevier.com/locate/calphad

Assessment of diffusion mobilities in FCC Cu–Ni alloys

J. Wang, H.S. Liu, L.B. Liu, Z.P. Jin*

School of Materials Science and Engineering, Central South University, Chang-Sha, Hunan, 410083, PR China

Received 8 May 2007; received in revised form 20 June 2007; accepted 14 August 2007
Available online 17 September 2007

Abstract

On the basis of the available thermodynamic parameters and experimental data of tracer diffusivity, intrinsic diffusivity and chemical diffusivity in the Cu–Ni binary system, the atomic mobilities of Cu and Ni in face-centered cubic (fcc) Cu–Ni alloys have been assessed as a function of temperature and composition using the CALPHAD approach and DICTRA software package. Comparisons between the calculated and measured diffusion coefficients show that most of the experimental information can be reproduced satisfactorily in the present work. The obtained mobility parameters can also predict reasonably the concentration profiles of the diffusion zone in binary Cu–Ni diffusion couple.

Keywords: Diffusion; Atomic mobility; CALPHAD; DICTRA; Cu–Ni alloys

1. Introduction

The Cu/Ni thin films have been used widely as an integral part of multilayer metallization on semiconductor chips and packages in the electronic industry [1–3]. Due to the miniaturization of modern devices and their stringent operating conditions, thin films governing the reliability of electronic packaging are becoming more critical than ever before. Microstructure evolution which results from the interdiffusion of elements across the interface between thin films during packaging and/or subsequent service of electronic devices may have significant influence on mechanical and electrical properties of electronic devices such as conductivity, bonding strength and adhesion [4–6]. Understanding better interdiffusion between thin films may help us to control the interfacial microstructure evolution and thus to predict the lifetime of electronic devices.

The software, DICTRA (DIffusion Controlled TRAnsformation), has been developed to simulate and predict microstructure evolution, which is an extension of the CALPHAD approach and operates under the CALPHAD framework [7–11]. This software is capable of applying thermodynamic and diffusion data to model diffusion-limited phenomena for multicomponent alloys. In this software, many material parameters such as thermodynamic and diffusion data must be involved. As a consequence, adequately accurate diffusion data are required during the simulation of microstructure evolution. The present work is to assess the atomic mobilities in face-centered cubic (fcc) Cu–Ni alloys through the DICTRA software package and thus to provide insight into diffusion characteristic with simulation of diffusion profiles by applying the assessed mobility parameters.

2. Experimental information

Extensive experimental investigations have been performed on diffusion phenomena in the Cu–Ni binary alloys. The selection of experimental data to assess atomic mobility depends mainly on whether the data from different investigations agree with each other or not. In Table 1, the experimental data that was selected in the present optimization has been listed.

Several investigations [12–14] have been performed to measure the impurity diffusion coefficients of Cu in pure Ni. Using the thin film technique and microprobe analysis, Helfmeier and Kniepmeier [12] have measured the impurity diffusion coefficients of Cu in pure Ni in the temperature range between 1048 and 1323 K. Helfmeier [13] has determined the impurity diffusion coefficients of Cu in pure Ni in the temperature range between 1014 and 1273 K through the microprobe analyzer to measure the Cu concentration gradient. Taguchi et al. [14] have employed the atomic absorption

---

* Corresponding author.
E-mail address: jin@mail.csu.edu.cn (Z.P. Jin).

0364-5916/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.calphad.2007.08.001

Table 1
Experimental diffusion data selected in the present optimization

Diffusion data	Method	Reference
Impurity diffusion coefficients	Microprobe analysis	Helfmeier and Kniepmeier [12]
	Microprobe analysis	Helfmeier [13]
	Atomic absorption analysis	Taguchi et al. [14]
Tracer diffusion coefficients	Residual activity technique	Anand et al. [15]
	Lathe sectioning technique	Monma et al. [16]
	Lathe sectioning technique	Anusavice and DeHoff [17]
	Lathe sectioning method	Ikushima [18]
	Lathe sectioning method	Mackliet [19]
	Lathe sectioning method	Anusavice et al. [20]
	–	Damköhler and Heumann [21]
Intrinsic diffusion coefficients	–	Damköhler and Heumann [21]
	–	Levasseur and Philibert [22]
	Foil method	Heumann and Grundhoff [23]
	Diffusion couple method	Iijima et al. [24]
Interdiffusion coefficients	Foil method	Heumann and Grundhoff [23]
	Diffusion couple method	Iijima et al. [24]

analysis to determine the impurity diffusion coefficients of Cu in pure Ni in the temperature range between 1080 and 1613 K. The impurity diffusion coefficients of Cu in pure Ni reported by [12–14] are compatible and have been employed in the present optimization.

The tracer diffusion coefficients of Cu and Ni in various Cu–Ni alloys have been reported by several authors [15–21]. Using Cu^{64} as a tracing element and applying the residual activity technique, Anand et al. [15] have determined the tracer diffusion coefficients of Cu in pure Ni for the temperature range 1123–1323 K. The tracer diffusion coefficients of Cu and Ni in various Cu–Ni alloys have been determined by Monma et al. [16] using Cu^{64} and Ni^{63} as tracing elements and applying the lathe sectioning technique in the temperature range from 1172 to 1340 K. Anusavice and DeHoff [17] have employed Cu^{67} and Ni^{66} as tracing elements and the lathe sectioning technique to measure the tracer diffusion coefficients of Cu and Ni in various Cu–Ni alloys in the temperature range between 1128 and 1328 K. Ikushima [18] and Mackliet [19] have investigated respectively the tracer diffusion coefficients of Ni in pure Cu using Ni^{63} as a tracing element and applying the lathe sectioning method in the different temperature ranges. However, Anusavice et al. [20] have used Ni^{66} as a tracing element and the lathe sectioning method to measure the tracer diffusion coefficients of Ni in pure Cu in the temperature range from about 1128 to 1328 K. Additionally, Damköhler and Heumann [21] have determined tracer diffusion coefficients of Cu and Ni in various Cu–Ni alloys using Cu^{64} and Ni^{57} as tracing elements at 1273 K. Experimental data about tracer diffusion coefficients mentioned above [15–21] are consistent and thus have been taken into account in the present optimization.

Intrinsic diffusion coefficients and interdiffusion coefficients in the Cu–Ni alloys have also been investigated by several authors [21–24]. Damköhler and Heumann [21] have determined intrinsic diffusion coefficients of Cu and Ni for Cu-rich Cu–Ni alloys up to 20 at% Ni at 1273 K. Levasseur and Philibert [22] have reported intrinsic diffusion coefficients of Cu and Ni in the Cu-rich Cu–Ni alloys at 1273 K. Intrinsic diffusion coefficients of Cu and Ni and interdiffusion coefficients have been measured by Heumann and Grundhoff [23] with the aid of the foil method over the complete concentration range at 1273 K. Iijima et al. [24] have used the diffusion couple method to determine interdiffusion coefficients and intrinsic diffusion coefficients of Cu and Ni in the concentration range from 25 to 80 at% Cu at 1273 K. The measured intrinsic diffusion coefficients and interdiffusion coefficients from different sources [21–24] are in reasonable agreement with each other within experimental error and have also been adopted in the present optimization.

3. Modeling of atomic mobility

The temporal profile of the diffusing species k is given by the Fick's law in the mass conservation form as follows:

$$\frac{\partial C_k}{\partial t} = -\mathrm{div}(J_k) \tag{1}$$

where C_k is the concentration in moles per volume, and div denotes the divergence operator. The diffusional flux of the species, J_k, in a multicomponent system is given by the Fick–Onsager law as:

$$J_k = -\sum_{j=1}^{n-1} D_{kj}^{n} \nabla C_j \tag{2}$$

D_{kj}^{n} is the chemical diffusion coefficient. The summation is performed over $(n-1)$ independent concentrations as the dependent n component may be taken as the solvent. D_{kj}^{n} in a substitutional solution phase which is given by the following expression [8,25]:

$$D_{kj}^{n} = \sum_{i} (\delta_{ik} - x_k) x_i M_i \left(\frac{\partial \mu_i}{\partial x_j} - \frac{\partial \mu_i}{\partial x_n} \right) \tag{3}$$

where δ_{ik} is the Kronecker delta ($\delta_{ik} = 1$ if $i = k$, otherwise $\delta_{ik} = 0$), x_i the mole fraction, μ_i the chemical potential of element i and M_i the composition dependent atomic mobility.

From the absolute-rate theory arguments, the mobility parameters M_i for the element i, can be divided into a frequency factor M_i^0 and an activation enthalpy Q_i. According to the suggestion by Jönsson [25,26], the M_i can be expressed as:

$$M_i = \exp\left(\frac{RT\ln M_i^0}{RT}\right)\exp\left(\frac{-Q_i}{RT}\right)\frac{1}{RT}{}^{mg}\Omega \tag{4}$$

where R is the gas constant, T the temperature, and ${}^{mg}\Omega$ is a factor taking into account a ferromagnetic contribution to the diffusion. Both M_i^0 and Q_i are temperature, composition and pressure dependent factors. Because the ferromagnetic effect for fcc phase can be ignored [27], combining $RT\ln M_i^0$ and Q_i into one parameter $\Delta G_i^* = RT\ln M_i^0 - Q_i$, Eq. (4) can be simplified to as:

$$M_i = \exp\left(\frac{\Delta G_i^*}{RT}\right)\frac{1}{RT}. \tag{5}$$

Similar to the phenomenological CALPHAD approach, Andersson and Ågren [8] suggested that the parameter ΔG_i^* should be assumed as a function of composition, which can be expressed by a Redlich–Kister polynomial [28]. For the fcc Cu–Ni alloys, ΔG_i^* is given as follows:

$$\Delta G_i^* = x_{\mathrm{Cu}}\Delta G_i^{\mathrm{Cu}} + x_{\mathrm{Ni}}\Delta G_i^{\mathrm{Ni}} + x_{\mathrm{Cu}}x_{\mathrm{Ni}}\sum_{j=0}^{n}\Delta^{(j)}G_i^{\mathrm{Cu,Ni}}(x_{\mathrm{Cu}} - x_{\mathrm{Ni}})^j \tag{6}$$

where $\Delta^{(j)}G_i^{\mathrm{Cu,Ni}}$ is the interaction term for diffusion between Cu and Ni. It is seen that M_i can be obtained through the available ΔG_i^*.

Assuming the mono-vacancy atomic exchange as the main diffusion mechanism, the tracer diffusivity D_i^* can be related to the atomic mobility M_i by the Einstein's relation:

$$D_i^* = RTM_i. \tag{7}$$

In a binary system, the tracer diffusivity D_i^* can be applied to calculate chemical diffusion coefficient $\tilde{D}$ by Darken's equation [29]:

$$\tilde{D} = (x_{\mathrm{B}}D_{\mathrm{A}}^* + x_{\mathrm{A}}D_{\mathrm{B}}^*)\phi \tag{8}$$

where ϕ is the thermodynamic factor, and can be expressed as:

$$\phi = 1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{A}}}{\mathrm{d}\ln x_{\mathrm{A}}} = 1 + \frac{\mathrm{d}\ln\gamma_{\mathrm{B}}}{\mathrm{d}\ln x_{\mathrm{B}}} = \frac{x_{\mathrm{A}}x_{\mathrm{B}}}{RT}\frac{\mathrm{d}^2G}{\mathrm{d}x^2} \tag{9}$$

where x_{A} and x_{B} are mole fractions of components A and B, respectively, γ_{A} and γ_{B} are the activity coefficients of components A and B, R is the gas constant and T is the temperature.

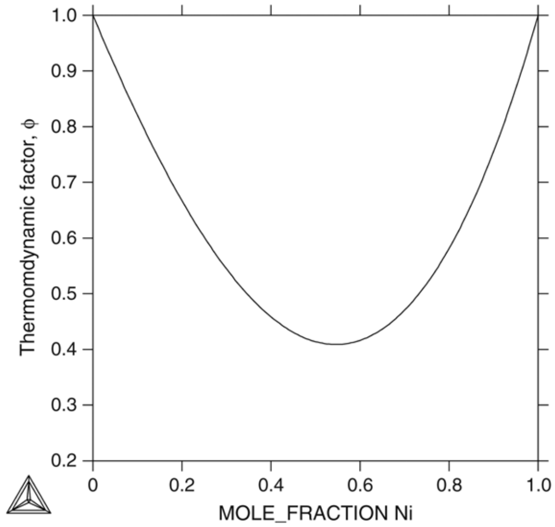

Fig. 1. Calculated thermodynamic factor (ϕ) of the fcc phase in the Cu–Ni binary system at 1273 K using the data from Mey [30].

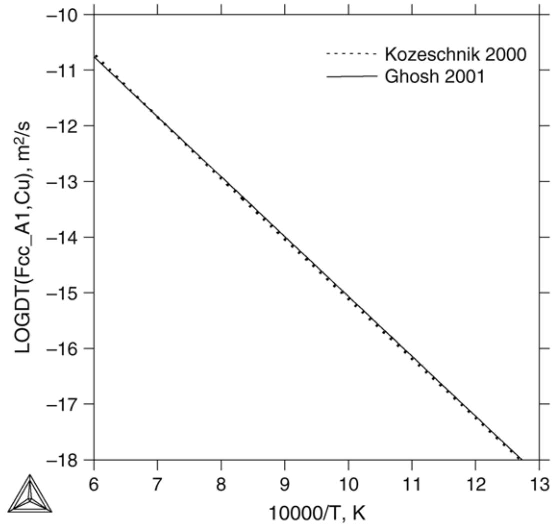

Fig. 2. Temperature dependence of self-diffusion coefficients of Cu calculated by Ghosh [31] and Kozeschnik [32].

Table 2
Mobility parameters of the Cu–Ni binary system for the face-centered cubic Cu–Ni alloys

Mobility	Parameters	Reference
Mobility of Cu	$\Delta G_{\mathrm{Cu}}^{\mathrm{Cu}} = -205\,872 - 82.5 \times T$	[31]
	$\Delta G_{\mathrm{Cu}}^{\mathrm{Ni}} = -250\,125 - 85.3 \times T$	This work
	$\Delta^0 G_{\mathrm{Cu}}^{\mathrm{Cu,Ni}} = +23\,887 - 17.7 \times T$	
Mobility of Ni	$\Delta G_{\mathrm{Ni}}^{\mathrm{Ni}} = -287\,000 - 69.8 \times T$	[33]
	$\Delta G_{\mathrm{Ni}}^{\mathrm{Cu}} = -232\,788 - 71.1 \times T$	This work
	$\Delta^0 G_{\mathrm{Ni}}^{\mathrm{Cu,Ni}} = +106\,790 - 75.4 \times T$	

4. Results and discussion

In order to calculate the thermodynamic factor (ϕ) during the assessment of mobility parameters, thermodynamic parameters for the fcc phase in the Cu–Ni binary system are necessary, which were taken directly from Mey [30]. Using these parameters, Fig. 1 presented the calculated thermodynamic factor (ϕ) of the fcc phase at 1273 K.

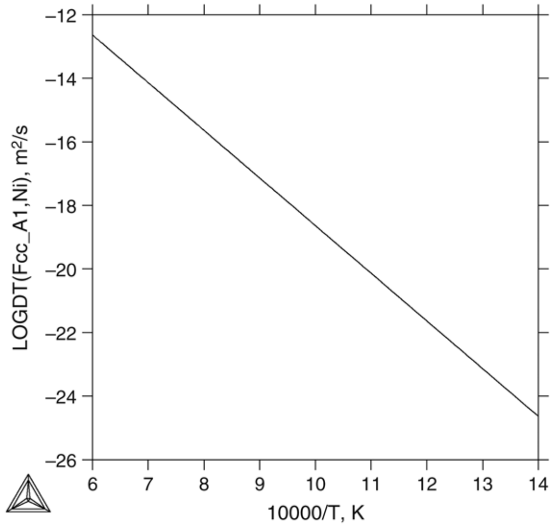

Fig. 3. Calculated temperature dependence of self-diffusion coefficients of Ni calculated by Jönsson [33].

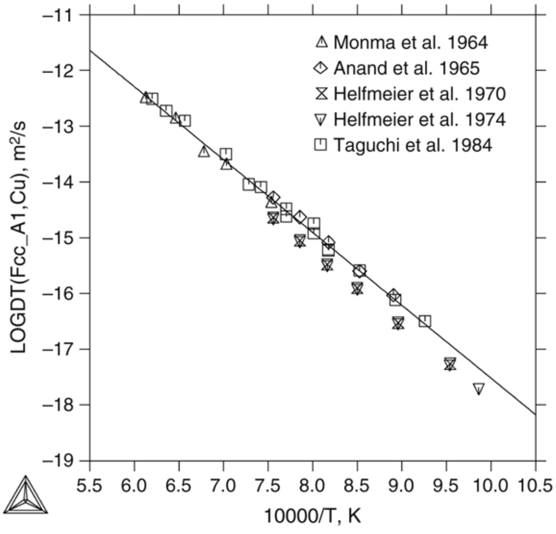

Fig. 4. Comparison between calculated temperature dependence of Cu tracer diffusion coefficients and experimental data [12–16] in pure Ni.

Ghosh [31] and Kozeschnik [32] have optimized the mobility parameters of Cu on the basis of experimental information on self-diffusivity of Cu. Fig. 2 shows the calculated temperature dependence of self-diffusivity of Cu. It is evident that the results calculated by Ghosh [31] and Kozeschnik [32] are in good agreement with each other. Furthermore, according to the available experimental data on the self-diffusivity of Ni, the mobility parameters of Ni have been assessed well by Jönsson [33], which can reproduce most of experimental data and are reasonable and self-consistent with extrapolation of high-order related systems. The temperature dependence of self-diffusivity of Ni calculated by Jönsson [33] has been illustrated in Fig. 3. Therefore the mobility parameters of Cu and Ni by Ghosh [31] and Jönsson [33] were adopted respectively in the present work.

All the optimizations for the atomic mobilities have been carried out in the PARROT module of the DICTRA software package [9,11]. Experimental data of tracer diffusion coefficients, intrinsic diffusion coefficients and interdiffusion coefficients have been employed to assess the mobility parameters of Cu and Ni for face-centered cubic Cu–Ni alloys. The mobility parameters obtained finally in the present work were listed in Table 2. However, note the temperature limits of the mobility parameters because all the experimental information used in the present optimization has been obtained at high temperatures (1000 K).

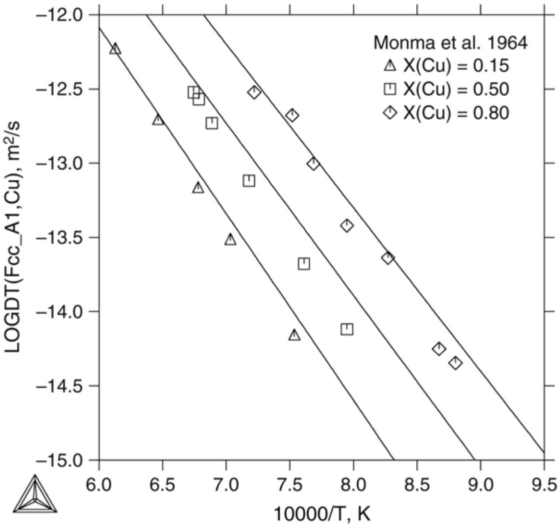

Fig. 5. Calculated temperature dependence of Cu tracer diffusion coefficients in comparison with experimental data [16] in various Cu–Ni alloys.

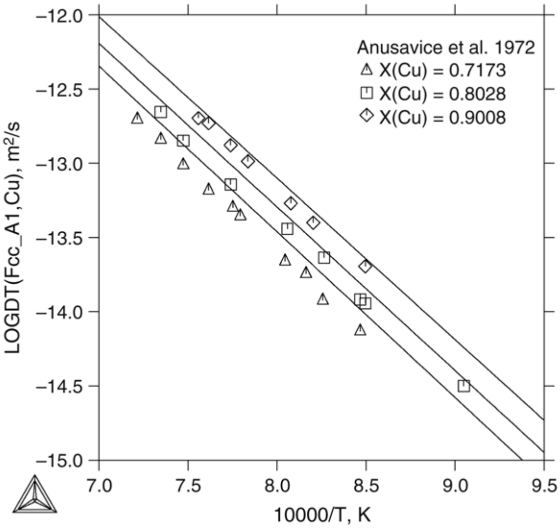

Fig. 6. Calculated temperature dependence of Cu tracer diffusion coefficients in comparison with experimental data [17] in various Cu–Ni alloys.

Fig. 4 illustrates the calculated temperature dependence of Cu tracer diffusion coefficients in pure Ni compared with experimental data [12–16]. The calculated values are in good accordance with experimental data reported by Taguchi et al. [14], Anand et al. [15] and Monma et al. [16], whereas a small difference exists between the measured data by Helfmeier and Kniepmeier [12] and Helfmeier [13] and the calculated values in the present work. Nevertheless, the calculated results

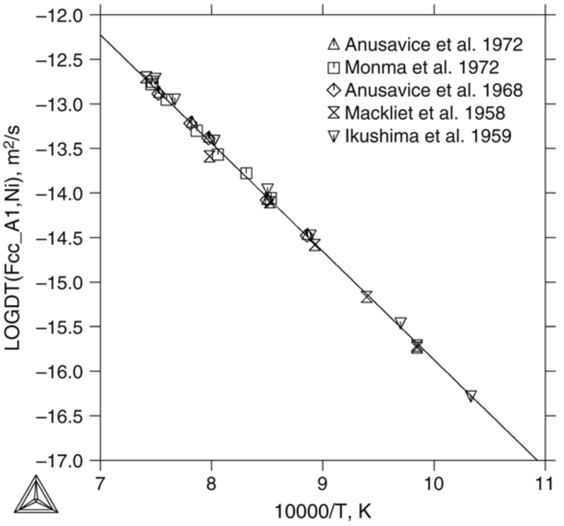

Fig. 7. Comparison of calculated temperature dependence of Ni tracer diffusion coefficients with experimental data [16–20] in pure Cu.

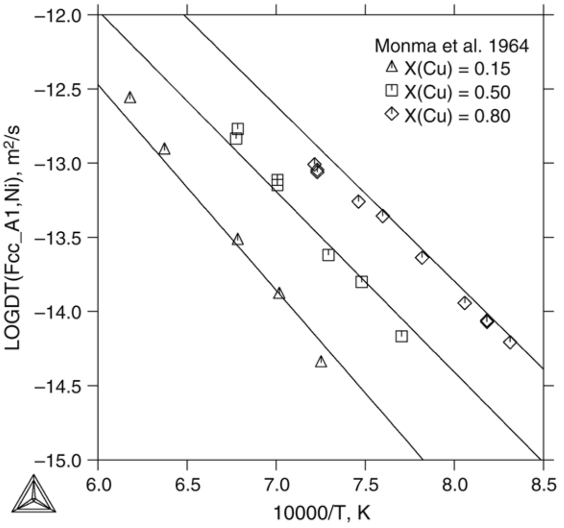

Fig. 8. Calculated temperature dependence of Ni tracer diffusion coefficients compared with experimental data [16] in various Cu–Ni alloys.

are still acceptable within experimental error. Comparisons between the calculated temperature dependence of Cu tracer diffusion coefficients in various Cu–Ni alloys and experimental data [16,17] were presented in Figs. 5 and 6. As can be seen (Figs. 5 and 6), the calculated results reproduce satisfactorily experimental data reported by Monma et al. [16] and Anusavice and DeHoff [17]. Fig. 7 shows the calculated temperature dependence of Ni tracer diffusion coefficients in pure Cu together with experimental data [16–20]. The calculated values are in excellent agreement with experimental data reported by Monma et al. [16], Anusavice and DeHoff [17], Ikushima [18], Mackliet [19] and Anusavice et al. [20]. Figs. 8 and 9 compared the calculated temperature dependence of Ni tracer diffusion coefficients in various Cu–Ni alloys with experimental data [16, 17]. It is evident that the calculated results in this work agree with the measured values by Monma et al. [16] and Anusavice and DeHoff [17]. In addition, Fig. 10 shows the calculated

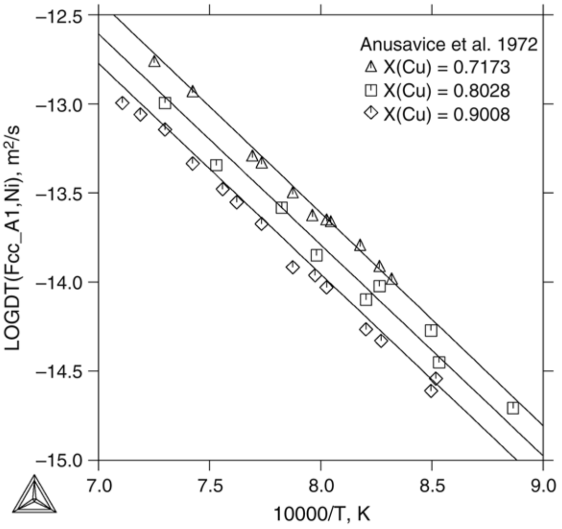

Fig. 9. Calculated temperature dependence of Ni tracer diffusion coefficients compared with experimental data [17] in various Cu–Ni alloys.

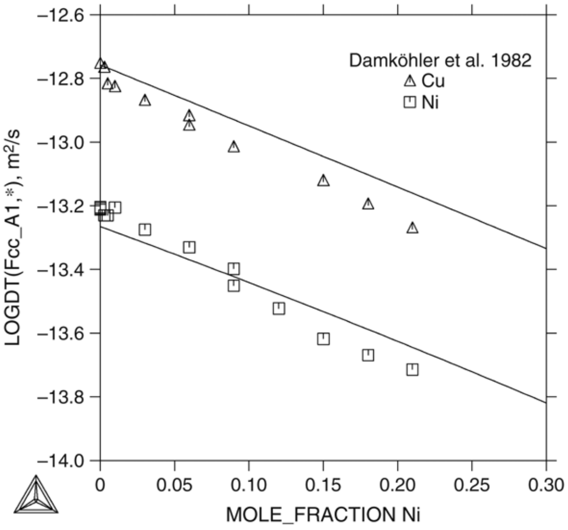

Fig. 10. Comparison of calculated tracer diffusion coefficients of Cu and Ni with experimental data [21] at 1273 K.

composition dependence of tracer diffusion coefficients for Cu and Ni compared with experimental data determined by Damköhler and Heumann [21] at 1273 K. The calculated tracer diffusion coefficients of Ni are in reasonable agreement with experimental data, while the calculated tracer diffusion coefficients of Cu show a small discrepancy. However, when considering experimental error, the calculated results in this work are still reasonable and acceptable.

Figs. 11 and 12 illustrates the calculated intrinsic diffusion coefficients of Cu and Ni compared with experimental data [21–24] at 1273 K, respectively. From Fig. 11, the calculated intrinsic diffusion coefficients of Cu are in accordance with experimental data measured by Damköhler and Heumann [21], Heumann and Grundhoff [23] and Iijima et al. [24] in the whole concentration range, but show a small discrepancy in the Cu-rich side compared with experimental data reported by Levasseur and Philibert [22]. Moreover, this problem is also

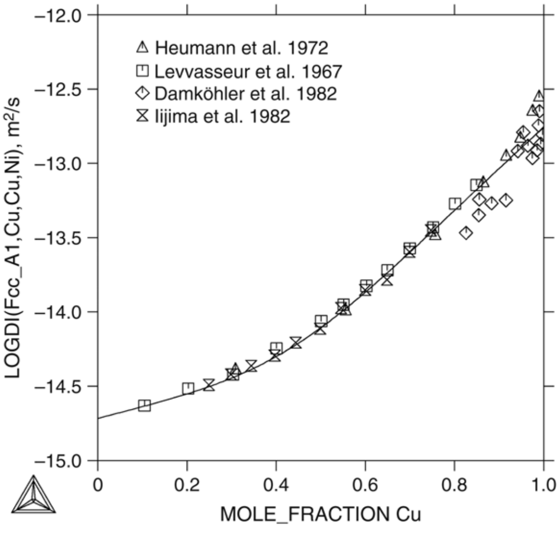

Fig. 11. Comparison between calculated intrinsic diffusion coefficients of Cu and experimental data [21–24] at 1273 K.

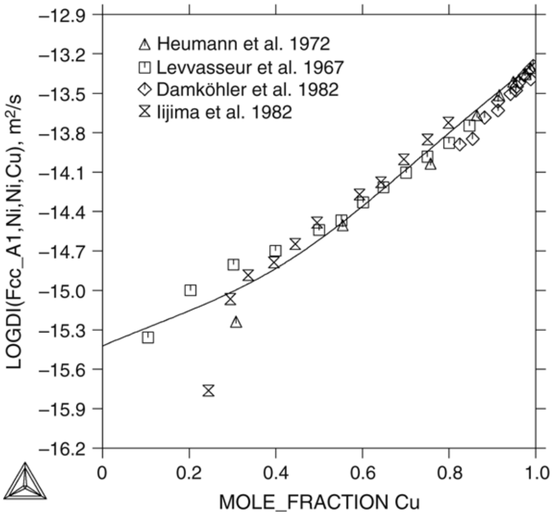

Fig. 12. Comparison between calculated intrinsic diffusion coefficients of Ni and experimental data [21–24] at 1273 K.

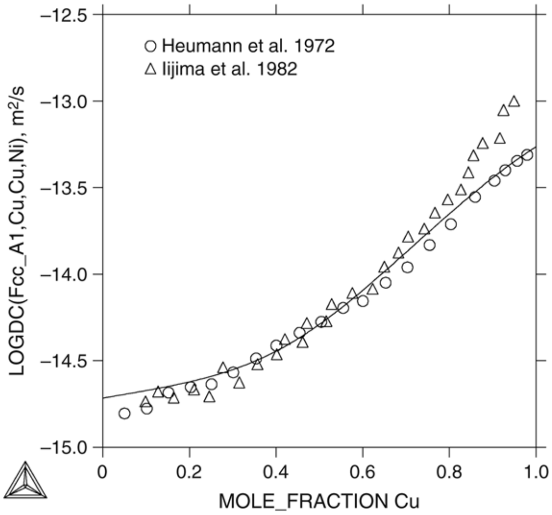

Fig. 13. Calculated interdiffusion coefficients compared with experimental data [23,24] at 1273 K.

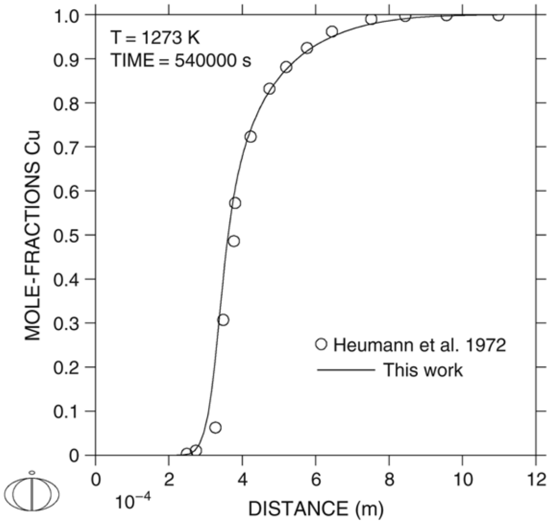

Fig. 14. Calculated concentration profiles of the binary Cu–Ni diffusion couple at 1273 K for 150 h together with experimental data [23].

found in Fig. 12. Meanwhile, the calculated intrinsic diffusion coefficients of Ni deviate with experimental data measured by Damköhler and Heumann [21], Heumann and Grundhoff [23] and Iijima et al. [24] in the Ni-rich side. Fig. 13 compared the calculated interdiffusion coefficients and experimental data [23, 24] at 1273 K. The calculated values agree with the data obtained by Heumann and Grundhoff [23], but show a little deviation with the data reported by Iijima et al. [24] in the Cu-rich side. The reason has been explained by Iijima et al. [24], who indicated that interdiffusion coefficients are apparently high in the Cu-rich side because of the formation of large Kirkendall voids.

The concentration profiles in the Cu/Ni diffusion couples were further modeled using the optimized mobility parameters through the DICTRA software package [9–11]. As shown in Fig. 14, the calculated results are in excellent agreement with experimental data at 1273 K for 150 h by Heumann and Grundhoff [23]. This confirms the validity of the mobility parameters obtained in the present assessment.

5. Conclusions

Combining the available thermodynamic and diffusion data with the CALPHAD approach, the atomic mobilities of Cu and Ni in face-centered cubic Cu–Ni alloys as a function of temperature and composition have been assessed using the DICTRA software package. The optimized mobility parameters can be employed to reproduce satisfactorily most of the experimental information on the measured diffusion coefficients in face-centered cubic Cu–Ni alloys and the concentration profiles for the Cu/Ni diffusion couple with reasonable accuracy can be predicted as well.

Acknowledgements

This work was financially supported by the National Science Foundation of China (Grant Nos. 50371104 and 50671122). One of the authors, H.S. Liu, would like to thank the Program for New Century Excellent Talents in University, China, for the financial support.

References

[1] P. Bai, B.D. Gittleman, B.-X. Sun, J.F. McDonald, T.-M. Lu, M.J. Costa, Appl. Phys. Lett. 60 (1992) 1824.
[2] C.Y. Liu, C. Chen, A.K. Mal, K.N. Tu, J. Appl. Phys. 85 (1999) 3882.
[3] N.N. Rammo, M.N. Makadsi, A.M. Abdul-Lettif, Phys. Status Solidi a 201 (2004) 3102.
[4] K. Zeng, K.N. Tu, Mater. Sci. Eng. R 38 (2002) 55.
[5] C.M.L. Wu, D.Q. Yu, C.M.T. Law, L. Wang, Mater. Sci. Eng. R 44 (2004) 1.
[6] T. Laurila, V. Vuorinen, J.K. Kivilahti, Mater. Sci. Eng. R 49 (2005) 1.
[7] J.-O. Andersson, L. Höglund, B. Jönsson, J. Ågren, in: G.R. Prudy (Ed.), Fundamentals and Applications of Ternary Diffusion, Pergamon Press, New York, 1990, p. 153.
[8] J.-O. Andersson, J. Ågren, J. Appl. Phys. 72 (1992) 1350.
[9] A. Borgenstam, A. Engström, L. Höglund, J. Ågren, J. Phase Equilib. 21 (2000) 269.
[10] L. Kaufman, H. Bernstein, Computer Calculation of Phase Diagrams, Academic Press, New York, 1970.
[11] B. Sundman, B. Jansson, J.-O. Andersson, CALPHAD 9 (1985) 153.
[12] H. Helfmeier, M. Feller-Kniepmeier, J. Appl. Phys. 41 (1970) 3202.
[13] H.U. Helfmeier, Z. Metallk. 65 (1974) 238.
[14] O. Taguchi, Y. Iijima, K. Hirano, J. Japan Inst. Met. 48 (1984) 20.
[15] M.S. Anand, S.P. Murarka, R.P. Agarwala, J. Appl. Phys. 36 (1965) 3860.
[16] K. Monma, H. Suto, H. Oikawa, J. Japan Inst. Met. 28 (1964) 192.
[17] K.J. Anusavice, R.T. DeHoff, Metal. Trans. 3 (1972) 1279.
[18] A. Ikushima, J. Phys. Soc. Japan 14 (1959) 1636.
[19] C.A. Mackliet, Phys. Rev. 109 (1959) 1964.
[20] K.J. Anusavice, J.J. Pinajian, K. Oikawa, R.T. DeHoff, Trans. Metal. Soc. AIME 242 (1968) 2027.
[21] R. Damköhler, T. Heumann, Phys. Status Solidi a 73 (1982) 117.
[22] J. Levasseur, J. Philibert, Phys. Status Solidi b 21 (1967) K1.
[23] V.T. Heumann, K.J. Grundhoff, Z. Metallk. 63 (1972) 173.
[24] Y. Iijima, K. Hirano, M. Kikuchi, Trans. Japan Inst. Met. 23 (1982) 19.
[25] B. Jönsson, Z. Metallk. 85 (1994) 498.
[26] B. Jönsson, Z. Metallk. 85 (1994) 502.
[27] B. Jönsson, Z. Metallk. 83 (1992) 349.
[28] O. Redlich, A. Kister, Ind. Eng. Chem. 40 (1948) 345.
[29] L.S. Darken, Trans. AIME 175 (1948) 184.
[30] S. Mey, CALPHAD 16 (1992) 255.
[31] G. Ghosh, Acta Mater. 49 (2001) 2609.
[32] E. Kozeschnik, Z. Metallk. 91 (2000) 57.
[33] B. Jönsson, Scand. J. Metall. 24 (1995) 21.