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Research article

Assessment of diffusional mobilities in bcc Cu–Sn and bcc Cu–Zn alloys

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Abstract: The Cu–Sn–Zn alloy system is technically very important. Brass (Cu–Zn) and bronze (Cu–Sn) alloys have been used and developed for tools and components for over thousands of years and are still used in a wide range of applications like marine components, bearings, music instruments and for components in contact with corrosive media. Even though it is a very old and well-studied alloy system, there are only few studies that analyze Cu–Sn–Zn coating systems. Furthermore very basic properties like the diffusion through different phases are not studied in detail. In this work experimental diffusion data in the literature is critically reviewed. On the basis of these studies a diffusion mobility database for the bcc phase of the ternary Cu–Sn–Zn is presented. The database was established using the DICTRA-type (DIffusion Controlled TRAnsformation) diffusion modeling. The resulting curves for the interdiffusion coefficient for various alloy concentrations are then compared to available literature data. Furthermore, experiments from diffusion couples are recalculated for validation. A good fit of these experimental data could be realized using only few parameters.

Keywords: copper alloys; diffusion; modeling

1. Introduction

Brass (Cu–Zn) and bronze (Cu–Sn) alloys have been used and developed for tools and components for over thousands of years. They are still technically very important. Alloys are used in a wide range of applications like marine components, bearings, music instruments and for components in contact with corrosive media. CuSnZn cast alloys, also known as gun metal, are used

for example for hydraulic parts, valves and gears and are resistant to steam and see water. Currently, processes are developed for the electrolytic deposition of coatings of the Cu–Sn–Zn system [1]. Electrolytes are available on the market under the name of "white bronze" coatings, but they suffer from a relatively thin achievable layer thickness, and therefore achieve only limited resistance against corrosion or wear. Furthermore, these electrolytes contain cyanide which is highly toxic. New coatings produced from cyanide-free electrolytes, which can achieve a good levelling, corrosion and wear properties, are under research [1]. In many cases, especially when using alloy combinations, diffusion plays a big role during production and use, for example during hot dip tinning of copper, the long term performance of white bronze coatings or joining of different copper alloys. The famous Kirkendall effect [2] that explains the mechanism of diffusion via a flux of vacancies has been performed on Cu–Cu/Zn diffusion couples. Thermodynamic and kinetic simulations allow calculating phase transformations and diffusion processes and can therefore support alloy development. The phases formed after the electrolytic coating process can be far from the thermodynamic equilibrium. Their long term stability and possible precipitation evolution can be calculated by simulations [3]. The DICTRA program has been developed to simulate and predict microstructure evolution within the CALPHAD (CALculation of PHAse Diagram) framework [4,5]. Using these methods, it is possible to simulate diffusion limited phenomena for multi-component alloys using thermodynamic and kinetic data. So far, there is one commercial thermodynamic database [6] and one mobility database [7] available for Cu-based alloys. In this commercial thermodynamic database many binary and ternary systems, including the Cu–Sn–Zn, are described, but only the mobility parameters in the fcc and the liquid phases were assessed. No mobility database for the bcc phase of this system is available. However, a description is needed for example to simulate β-phase containing CuZn alloys.

The aim of the present work is to assess the atomic mobilities of bcc Cu–Sn and bcc Cu–Zn alloys as a function of temperature and composition with the use of DICTRA. The prediction of diffusion profiles is also presented by applying the assessed mobility parameters.

2. Materials and method

The main challenge of the present work lays in the fact that the bcc Cu, bcc Sn, bcc Zn, bcc Cu–Sn and bcc Cu–Zn phases are unstable at room temperature. The Cu–Sn system shows a narrow composition and temperature range where the bcc phase is stable. These thermodynamic characteristics hinder the feasibility of acquiring experimental mobility data. Therefore, information for assessing and validating mobility parameters are scarce. To counter these limitations, theoretical and empirical relations are employed on the basis of i.e. self- and impurity- diffusivity. By using the limited available data and using the framework of Thermo-Calc and CALPHAD/DICTRA, it is possible to extrapolate the information to concentration and temperature ranges where only limited experimental data is available.

2.1. Atomic mobility and diffusivity

For a substitutional solution containing n components, referred to the volume-fixed frame of reference, the diffusion flux of species k (J_k) is given by the Fick–Onsager law [8] as shown in Eq 1:

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

D_{kj}^n is the inter-diffusion coefficient and ∇C_j is the concentration gradient of species j. The summation is performed over $(n-1)$ independent concentrations with the dependent n elements taken as the solvent. The temporal profile of the species k, $\left(\frac{\partial C_k}{\partial t}\right)$, is governed by the mass conservation law, being described by Eq 2:

$$\frac{\partial C_k}{\partial t} = -\nabla \times J_k \tag{2}$$

Referring to the volume-fixed frame of reference, for a substitutional component j, the diffusivities of the form D_{kj}^n are products of a pure thermodynamic factor, $(\partial \mu_i / \partial x_j)$ and a kinetic one, which can be viewed as a simplified term of proportionality depending on the mobility M_i of each element i as proposed by Andersson and Ågren [9], shown in Eq 3:

$$\widetilde{D}_{kj}^n = \sum_{i=1}^{n} (\delta_{ik} - x_k) x_i M_i \left(\frac{\partial \mu_i}{\partial x_j} - \frac{\partial \mu_i}{\partial x_n}\right) \tag{3}$$

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 and M_i the atomic mobility of element i.

Taking a general binary substitutional phase containing elements A and B into consideration, like the bcc-Cu phase. As in the CALPHAD method framework, the mobility M_i for the elements i ($= A$ or B) can be divided into a frequency factor M_i^0 and an activation enthalpy Q_i. From the absolute-rate theory arguments, M_i can be given by Eq 4 [10]:

$$M_i = exp\left(\frac{\text{RTln}(M_i^0)}{RT}\right) exp\left(\frac{-Q_i}{RT}\right) \frac{1}{RT} = \frac{1}{RT} exp\left(\frac{\Phi_i}{RT}\right) \tag{4}$$

where Φ_i is a composition-dependent property; R is the gas constant and T the current temperature. In the CALPHAD treatment, for a bcc binary alloy, Φ_i is expanded with a Redlich–Kister [11] polynomial as shown it Eq 5:

$$\Phi_i = x_A \Phi_i^A + x_B \Phi_i^B + x_A x_B \sum_r {}^r \Phi_i^{A,B} (x_A - x_B)^r \tag{5}$$

where Φ_i^A, Φ_i^B and ${}^r\Phi_i^{A,B}$ are the model parameters to be evaluated from experimental data in this work; x_A and x_B are the molar fractions of A and B, respectively; r is the Redlich–Kister polynomial order.

The tracer diffusion coefficients (D_i^*) for A and B, can be related to the mobility by the

Einstein's relation [12], Eqs 6 and 7, respectively:

$$D_A^* = RTM_A \tag{6}$$

$$D_B^* = RTM_B \tag{7}$$

Also, the intrinsic diffusion coefficients for A and B that characterize the diffusion rates of elements on the lattice reference frame (D_i^I), can be expressed by Eqs 8 and 9:

$$D_A^I = D_A^* F \tag{8}$$

$$D_B^I = D_B^* F \tag{9}$$

where the superscript I denotes the intrinsic reference frame or the lattice reference frame. F is the thermodynamic factor defined by Eq 10:

$$F = \frac{x_A x_B}{RT}\left(\frac{\partial^2 G_m}{\partial^2 x_A} + \frac{\partial^2 G_m}{\partial^2 x_B} - 2\frac{\partial^2 G_m}{\partial x_A \partial x_B}\right) \tag{10}$$

where G_m is the molar Gibbs free energy of a substitutional phase.

In the binary system, we can calculate inter-diffusion coefficient $\widetilde{D}$ by Darken's equation [13], Eq 11, by applying the tracer diffusion coefficients:

$$\widetilde{D} = (x_A D_A^I + x_B D_B^I) = (x_A D_A^* + x_B D_B^*)F \tag{11}$$

2.2. Self-diffusion in bcc phases

During optimization, the self-diffusivity in each pure bcc phase is necessary. Bcc-Cu, bcc-Sn and bcc-Zn are not stable under ambient conditions. For this reason, it is almost impossible to obtain the self-diffusivity in these phases by means of experimental methods and such data are rarely found in the literature. To overcome this problem, theoretically self-diffusion coefficients for diffusion in metallic systems can be calculated by the use of the Langmuir–Dushman relation [14] (Eq 12):

$$D = \frac{Qa^2}{N_0 h}e^{-\frac{Q}{RT}} \tag{12}$$

where a is the lattice constant, N_0 is the Avogadro's number, and h is Planck's constant. In general, a good agreement is found from the Langmuir–Dushman equation for the activation energy when applied to many systems of diffusion metal pairs. It's very simple form provides the opportunity to predict diffusivity in some instable structures. Additionally to this concept, the Askill's [15] semi-empirical relationship is commonly used to evaluate the activation energy for self-diffusion in metastable or instable phases and is expressed as shown in Eq 13:

$$Q = RT_m(K + 1.5V) \tag{13}$$

where K is the crystal structure factor ($K = 13$ for bcc). T_m is the melting temperature. In cases in which the phase is unstable T_m can be derived from the SGTE thermodynamic database by Dinsdale [16]. V is the valence. According to electronic configurations of the elements, Han et al. [17]

and Wang et al. [18] estimated the valance and lattice parameters of the unstable Cu, Sn and Zn bcc phases by using the density functional theory (DFT) methods. Moreover, they calculated the T_m of the unstable bcc Cu, Sn and bcc Zn from the thermodynamic database established by Dinsdale [16] by intersecting the curves of the liquid and bcc phases and finally combined these values with the Askill's semi-empirical relationship (Eq 13) and Langmuir–Dushman equation (Eq 12) to determine the self-diffusion coefficient in bcc structures. Their finds were taken into account in this work and used as parameters to the self-diffusion Cu, Sn and Zn bcc phases.

2.3. Evaluation of experimental diffusion data

Mobility parameters for the copper based β phase (bcc) are hardly found in the literature due to its instability at room temperature and its small solubility field in the Cu–Zn–Sn system. Despite the lack of experimental data, the diffusion process in the β phase is of importance because of its presence during the solidification of Cu–Sn–Zn alloys [19] and due to the usage of β brass in various applications. Miettinen [19] reported a thermodynamic-kinetic model of copper alloys dedicated to simulate the solidification of Cu–Sn–Zn alloys. In this work, the impurity diffusion of Sn and Zn in pure bcc-Cu were adopted using the optimization functions from [19]. The phase fraction factor was then extrapolated to the level of infinite dilution of the solute. According to Eq 5, the impurity diffusion of Cu in the hypothetical bcc-Sn and bcc-Zn phases are parameters required to the optimization and cannot be measured experimentally as explained above. It is assumed that the difference of both the frequency factor and the activation enthalpy between the self-diffusion and the impurity diffusion of the stable bct-Sn and hcp-Zn structures is the same as for the bcc-Sn and bcc-Zn crystal structure. A linear estimation of to the impurity-diffusion of Cu in these bcc phases was done by adding those differences to self-diffusion parameter of bcc-Sn and bcc-Zn. The inter-diffusion coefficients ($\widetilde{D}$) and intrinsic diffusion measured by Yokota M and Landergren S [20,21] where included and used to optimize the diffusion mobility interaction parameter. The selection of the experimental diffusion data is presented the following two subsections.

Landergren et al. [21] measured the diffusion coefficients and marker movements in β brasses using weld couples and alloys. In their work, pure copper was obtained by electrodeposition of copper on Cu–Zn samples in the composition range from 43.5 to 49 atomic percent of zinc, with a deviation of ±0.2 at% Cu. The diffusion coefficients were measured for all of the couples which were heat treated at 500, 600, 700 and 800 °C. Yokota et al. [20] measured the inter-diffusion coefficient in the β Cu–Sn phase by the Boltzmann–Matano method at temperatures of 874, 907, 926, 973 and 933 K using diffusion couples consisting of commercially pure copper and β Cu–Sn alloys with Sn content varying from 13.5 to 15.5 at%. This study shows that the inter-diffusion coefficients increase with the Sn content in the β phase and that the Cu atom diffuses faster than the Sn atom in these alloys.

2.4. Optimization procedure

The thermodynamic factor of diffusion can be readily calculated from thermodynamic parameters. Gierlotka et al. [22] have reported an assessment of the Cu–Sn–Zn ternary system. Focusing on the liquid projection of the Cu–Sn–Zn system, the thermodynamic parameters of the

Cu–Sn binary system assessed by Gierlotka W differs from the ones previously assessed by Jantzen & Spencer [23]. Although Gierlotka et al. assessment of the Cu–Zn shows good agreement with high temperature experimental values, some interaction parameters related to the bcc phase of the Cu–Zn system lead to the prediction of intense solubility even for temperature ranges we expect the bcc phase to be ordered. Jetzen & Spenser used lower temperature experimental data of the bcc-fcc Cu rich corner equilibrium and when using their interaction parameters related to the bcc phase of the Cu–Zn, lower solubility is predicted. Moreover, Gierlotka et al. used up to 3rd order Redlich–Kister parameters to describe the Cu–Zn excess Gibbs energy of mixing while Jantzen & Spencer [23] could have good agreements only up to 2nd order terms. As these parameters influence in the aim of this work, we had to choose the more convenient to be used. Therefore, parameters assessed by Jantzen & Spencer were taken into account and used on the bcc Cu–Zn diffusivity assessment expecting to be congruent with possible future thermodynamic and kinetic data. The thermodynamic parameters were used in this work and are presented in Table 1. A description of the thermodynamic modelling can be found in [4], the parameters are described in more detail in [22,23].

Table 1. Thermodynamic parameters of the Cu–Zn and Cu–Sn binary system for the body centered cubic Cu–Zn and Cu–Sn alloys.

Phase	Model	Parameters (J mol^{-1})	Ref.
bcc	(Cu,Zn)$_1$(Va)$_3$	$^0L^{bcc}_{Cu,Zn:Va} = -51595.87 + 13.06392 \times T$	[23]
		$^1L^{bcc}_{Cu,Zn:Va} = 7562.13 - 6.45432 \times T$	[23]
		$^2L^{bcc}_{Cu,Zn:Va} = + 30743.74 - 29.91503 \times T$	[23]
bcc	(Cu,Sn)$_1$(Va)$_3$	$^0L^{bcc}_{Cu,Sn:Va} = -41774.195 + 47.8773 \times T$	[22]
		$^1L^{bcc}_{Cu,Sn:Va} = -12316.502 - 50.4458 \times T$	[22]

Neumann and Tuijin [24] reported the impurity diffusion of Cu and the self-diffusion coefficients of Sn and Zn in in pure bct-Sn and hcp-Zn. These values, the theoretical calculation of self-diffusion in the hypothetical bcc-Sn and bcc-Zn proposed in the section 2.2 and the estimation of the impurity diffusion of Cu in hypothetical bcc-Sn and bcc-Zn, reported in the section 3, are summed up in Table 2.

Table 2. Impurity diffusion of Cu and self-diffusion of Sn and Zn in the bct-Sn and hcp-Zn phases and estimated values of Cu impurity-diffusion in hypothetical pure bcc-Sn and bcc-Zn.

Diffusing element	bct-Sn		bcc-Sn		Diffusing element	hcp-Zn		bcc-Zn	
	Q	D$_0$	Q	D$_0$		Q	D$_0$	Q	D$_0$
	(J mol^{-1})	(m^2 s^{-1})	(J mol^{-1})	(m^2 s^{-1})		(J mol^{-1})	(m^2 s^{-1})	(J mol^{-1})	(m^2 s^{-1})
Sn	−22800	1.4×10^{-4}	−40300	1.5×10^{-5}	Cu	−125300	2.0×10^{-4}	−94940	1.91×10^{-4}
Cu	−33020	2.4×10^{-7}	−50520	3.61×10^{-7}	Zn	−97900	2.6×10^{-5}	−67540	1.7×10^{-5}

Based on the selected necessary parameters and on the experimental data presented in sections 3.1 and 3.2, the experimental inter-diffusion coefficients were optimized using the PARROT module of the DICTRA software in order to obtain the interaction parameters $Q^{Cu,Zn}_{Zn}$ and $Q^{Cu,Sn}_{Sn}$.

3. Results

In the past few decades, some researchers have investigated diffusion phenomena in binary bcc Cu–Zn and Cu–Sn alloys. Landergren et al. and Yokota et al. [20,21] have reported the measured interdiffusion coefficients of these systems. These results coupled with the thermodynamic framework reported in the studies from Gierlotka [22] and Spencer [23] and theoretical calculations allows the mobility parameters of the Cu–Zn and Cu–Sn system to be optimized via DICTRA software. The mobility parameters assessed in the present work are summarized in Table 3.

Table 3. Mobility parameters for the bcc phase of the Cu–Sn–Zn ternary system.

Mobility		Parameters (J mol^{-1})	Ref.
Cu	Φ_{Cu}^{Cu}	$-151800 - 79 \times T$	[18]
	Φ_{Cu}^{Sn}	$-50520 + R \times T \times LN(3.61E\text{-}07)$	Estimated in this work
	Φ_{Cu}^{Zn}	$-94940 + R \times T \times LN(1.91E\text{-}04)$	Estimated in this work
	$\Phi_{Cu}^{Cu,Zn}$	$-37389.47 + 11.99 \times T$	Optimized in this work
	$\Phi_{Cu}^{Cu,Sn}$	$123250.6 + 123.45 \times T$	Optimized in this work
Zn	Φ_{Zn}^{Cu}	$-151958 + R \times T \times LN(4.23E\text{-}06)$	[19]
	Φ_{Zn}^{Zn}	$-67540 + R \times T \times LN(1.7E\text{-}05)$	[17]
	$\Phi_{Zn}^{Cu,Zn}$	$123353.37 - 77.60 \times T$	Optimized in this work
Sn	Φ_{Sn}^{Cu}	$-156195 + R \times T \times LN(4.277E\text{-}04)$	[19]
	Φ_{Sn}^{Sn}	$-40300 + R \times T \times LN(1.5E\text{-}05)$	[17]
	$\Phi_{Sn}^{Cu,Sn}$	$293195.93 - 257.9 \times T$	Optimized in this work

4. Discussion

4.1. The Cu–Zn system

The results of the optimization can be seen in Figure 1, which shows a good agreement of the calculated inter-diffusion coefficients with experimental data from Landergren [21].
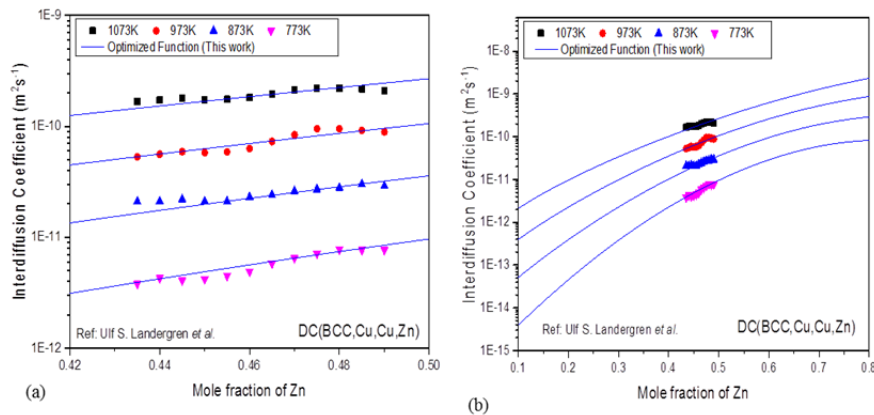

Figure 1. Comparison between the calculated and measured inter-diffusion coefficients of Cu–Zn alloys at different temperatures in the a) range of interest and b) full range.

As can be seen in Figure 1, the inter-diffusion coefficients rise as the amount of Zn increases. This behavior is more pronounced at 773 K than for the other temperatures which is consistent with the experimental data. A comparison of the calculated Zn concentration profile and experimentally measured data from Resnick and Balluffi [25] are shown in Figure 2, where the simulation for the penetration curve of the Zn/Cu diffusion couple annealed at 873 K for 7200 s (2 h) and at 973 K for 59400 s (16.5 h) are shown. As can be seen, the concentration profiles are all in excellent accordance with the experimental data.
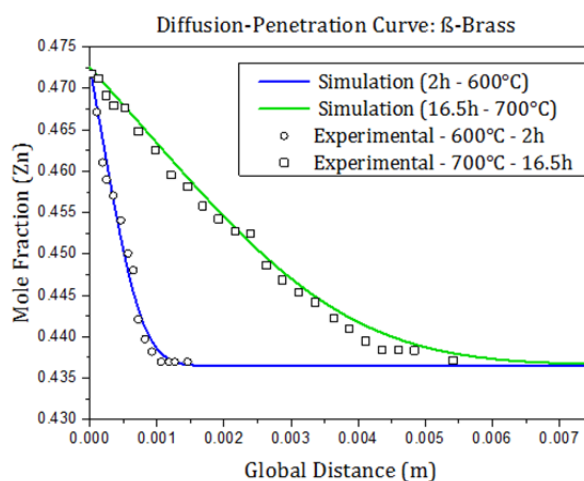
Figure 2. Diffusion-penetration curves for β brass vapor solid couples at 600 °C for 2 h and 700 °C for 16.5 h. Dots are experimental results obtained by Resnick and Balluffi [25] and solid lines are the simulation results calculated using the database assessed in this work.

4.2. The Cu–Sn system

A comparison of the experimental data from Yokota [20] superimposed with the calculated curves using the assessed parameters in this work is shown in Figure 3.

It is apparent that good agreement is obtained for the temperature range from 926 to 993 K. However, the agreement is less satisfactory for lower temperatures in the range of 874 to 907 K, where one can note that the numerical values optimized in this work are close to the experimental results, but the trend of the curve with Sn contents higher than 1.5 at% is not reproduced correctly. The experimental results also show a high dependence of the interdiffusion coefficient with the Sn content.

One can see in Figure 3b that the values of the interdiffusion coefficients show a constant behavior after a certain amount of Sn, around 3 at% Sn. This shape is a result of the underlying Gibbs energy curve of the bcc phase used in this work. To illustrate that influence, Figure 4 shows the curves of the Gibbs energy for 993 and 874 K.
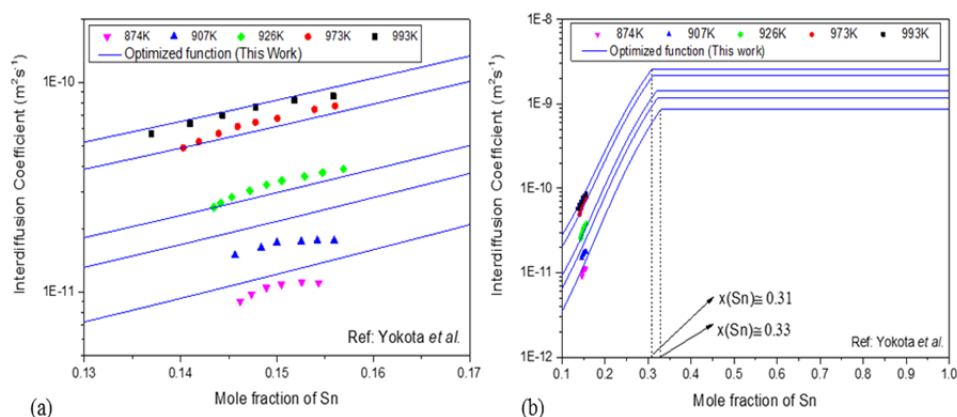
Figure 3. Comparison between the calculated and measured inter-diffusion coefficients of Sn–Zn alloys at different temperatures in the a) range of interest and b) full range.
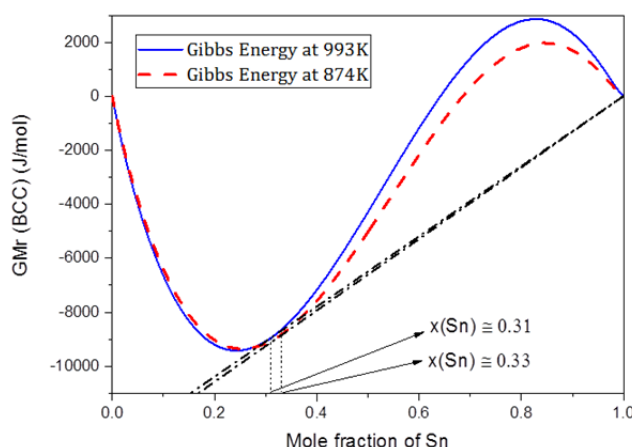

Figure 4. Calculated Gibbs energy referenced to the β phase on the Cu–Sn system with Sn content at different temperatures. The tangent law is marked with dashed lines.

The underlying Gibbs energy functions from Gierlotka et al. [22] were not critically reviewed in this work. Using different Gibbs energy functions as a basis for the diffusion simulations may also lead to different mobility parameters. Due to no experimental composition profiles for the bcc Cu–Sn alloy no further validation could be done up to the present moment. Despite of this difficulties, we can roughly compare the calculated inter-diffusivities in the extrapolated Cu-rich metastable bcc Cu–Sn alloy with the inter-diffusivities of the stable Cu–Sn fcc phase data reported by Xu HX and Zhang LJ [26]. For same temperature and similar composition, 973 K and 0.1 atomic fraction of Sn, the inter-diffusivity in fcc Cu–Sn alloy is around $10^{-13.5} \, m^2 \, s^{-1}$ while for bcc Cu–Sn alloy the value is around $2 \times 10^{-11} \, m^2 \, s^{-1}$. This difference seems reasonable since quantity values are relatively close from each other and because the bcc packing factor is 0.74 while for the fcc it is 0.68, i.e. for substitutional diffusion an atom would face a more compact path to diffuse into the fcc phase and thus lowering its velocity. The comparison is somehow rough since no other physico- and thermo-chemical behavior of the different phases were taken into account. In order to improve the validation and accuracy of the parameters, experiments such as penetration curves and diffusion

couples on the Cu–Sn system are suggested.

5. Conclusion

The experimental diffusion data was assessed to develop diffusion mobility data for the bcc phase of the Cu–Zn and Cu–Sn binary systems by using the DICTRA software and optimized via its PARROT-module. Overall, satisfactory agreements were obtained between the calculated diffusion coefficients and the available experimental values. The developed diffusion mobility database, in conjunction with the thermodynamic description, has been successfully used to predict binary diffusion couple experiments. The optimized mobility parameters can also be used to simulate and reproduce diffusion controlled processes for Cu–Zn and Cu–Sn alloys in the range of temperatures studied.

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Conflict of interests

There is no conflict of interests between authors.

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