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Letter to Editor

INTERDIFFUSION COEFFICIENT AND ATOMIC MOBILITY FOR FCC Ag-Cu-Mg PHASE AT 1073 K

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Abstract

In this work, the interdiffusion coefficient and atomic mobility for the fcc Ag-Cu-Mg phase at 1073 K were investigated by combining diffusion couple experiments and calculations. Based on the experimental composition profiles, the diffusion coefficients at the intersections of the diffusion paths were calculated using the Matano-Kirkaldy method. Using the thermodynamic descriptions available in the literature, the atomic mobilities for the fcc Ag-Cu-Mg phase were automatically optimized by numerical inverse method integrated with the CALTPP (CALculation of ThermoPhysical Properties) program. Moreover, the obtained atomic mobilities were confirmed to be reliable by good agreements between the model-simulated and the measured composition profiles. In addition, three-dimensional surfaces were presented for the interdiffusion coefficient, activation energy, and frequency factor. The presently obtained atomic mobilities can be incorporated into the diffusion database for Ag-based alloys, which can contribute to microstructure simulation and materials design.

Keywords: *Fcc Ag-Cu-Mg; Interdiffusion coefficient; Atomic mobility; CALTPP; Activation energy; Frequency factor*

1. Introduction

Silver and its alloys are widely used in the form of circuit board, conductive element, electronic industries, machinery manufacturing, and other fields due to their good thermal stability and excellent conductivity [1-3]. The Ag-Cu alloy has a good electrical conductivity and thermal conductivity [4]. While the addition of Mg can reduce the recrystallization temperature and increase the hardness of the silver alloy [5-8]. Therefore, the Ag-Cu-Mg system is a key sub-system for Ag-based alloys and is therefore selected as the research object in this work.

The investigations on the diffusion kinetics are basis for simulating the microstructure evolution during materials process and service [9, 10]. So far, no research work has been done on studying diffusion kinetics for the Ag-Cu-Mg system. Hence, it is necessary to investigate the diffusion behavior in the Ag-Cu-Mg system. It should be noted that in order to efficiently obtain the interdiffusion coefficient and atomic mobility for alloys, we recently developed one intelligent program i.e. CALTPP (CALculation of ThermoPhysical Properties) [11], which can be applied to the calculations and predictions for the thermophysical properties (including diffusion coefficient, interface energy, thermal conductivity, viscosity and molar volume) of multi-element alloys [11] varying with composition and temperature. The diffusion module is mainly utilized to evaluate the diffusion kinetics parameters of multi-component alloy system and simulate the diffusion process, which incorporates the high-throughput calculation method called numerical inverse method. This module has been verified to be reliable and efficient by applying it to several systems [11-13]. In the present work, we utilize the CALTPP program to investigate the diffusion kinetics for fcc Ag-Cu-Mg phase.

The main aims in this work are as follows: (i) to measure the composition profiles through diffusion couple experiments; (ii) to optimize and verify the atomic mobilities in fcc Ag-Cu-Mg phase by CALTPP program based on the measured composition profiles together with the thermodynamic descriptions, and (iii) to present three-dimensional diagrams for interdiffusion coefficient, activation energy, and pre-frequency factor by means of the presently established atomic mobilities.

2. Experiments

Ag (purity: 99.99 wt%), Cu (purity: 99.99 wt%),

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and Mg (purity: 99.99 wt%) were used as starting materials. The samples of Ag-Cu alloys were arc melted under an Ar atmosphere using a non-reactive W electrode. The buttons were re-melted four times to improve their homogenization. The Ag-Mg alloys were prepared as buttons in a vacuum induction melting furnace under an Ar atmosphere. Since the melting point of Cu is close to the boiling point of Mg, Ag-Cu alloy was prepared by using a vacuum arc furnace firstly, and then it was fused with pure Mg in an induction furnace to obtain the desired Ag-Cu-Mg alloy. After that, the buttons were linearly cut into blocks of approximate dimensions of 5×2.5×8 mm^3 and sealed into an evacuated quartz tube, which were then homogenized at 1073 ± 5 K for 20 days. After polishing and cleaning, all blocks were bound together with Mo clamps to obtain four diffusion couples for annealing at 1073K for 24 hours. After standard metallographic technique, the composition profiles for all diffusion couples were determined using EPMA (Electron Probe MicroAnalysis) technique. The terminal compositions, annealing temperature and diffusion time of the presently prepared diffusion couples are listed in Table 1.

Table 1. *List of terminal compositions, annealing temperature and diffusion time of the diffusion couples in the present work*

Couple	Composition (at.%)	Temperature (K)	Diffusion time (hours)
A1	Ag/Ag-2.1Cu-9.9Mg	1073	24
A2	Ag/Ag-4.1Cu-4.7Mg	1073	24
A3	Ag-2.0Cu/Ag-5.1Mg	1073	24
A4	Ag-3.9Cu/Ag-9.9Mg	1073	24

3. Results and discussion

One representative BSE (Back Scattered Electron) figure for diffusion couple A3 is presented in Fig. 1, indicating that the presently prepared diffusion couple is of single-phase. For the calculations of interdiffusion coefficient and atomic mobility, we used both the Matano-Kirkaldy method and the novel numerical inverse method for cross validations. Both methods are incorporated in our recently developed CALTPP program. One can refer to Ref. [12] for detailed descriptions of these two methods.

The evaluation of atomic mobilities for fcc Ag-Cu-Mg phase is carried out by the numerical inverse method incorporated in CALTPP program. We input the EPMA-measured composition profiles, the thermodynamic descriptions [14, 15] and the atomic mobilities for sub-binary systems [4, 16-19] into CALTPP program. Then CALTPP program can automatically evaluate $\Phi_{Cu}^{Ag,Mg}$ and $\Phi_{Mg}^{Ag,Cu}$. The presently obtained atomic mobilities for fcc Ag-Cu-Mg phase are listed in Table 2. It is stressed that other commercial diffusion software packages cannot evaluate the atomic mobilities automatically.

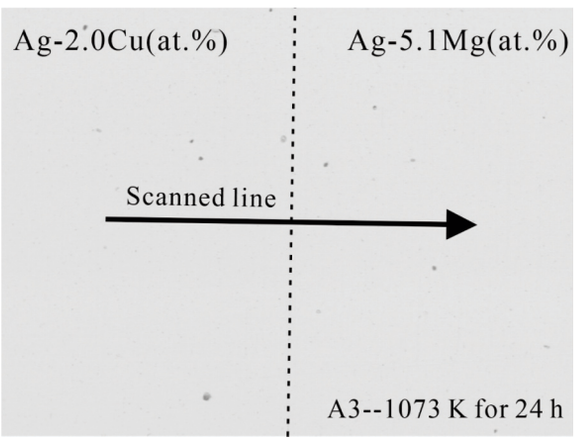

Figure 1. *The representative BSE figure for diffusion couple A3*

Table 2. *List of the atomic mobilities in fcc Ag-Cu-Mg phase*

Mobility	Parameters, J/mol	References
Mobility of Ag	$\Phi_{Ag}^{Ag} = -175892.05 - 93.05 \cdot T$	[16]
	$\Phi_{Ag}^{Cu} = -192886.08 - 81.68 \cdot T$	[4]
	$\Phi_{Ag}^{Ag,Cu} = 460892.85$	[4]
	$\Phi_{Ag}^{Ag,Mg} = 162630.13 + 61.87 \cdot T$	[17]
Mobility of Cu	$\Phi_{Cu}^{Cu} = -205872 - 82.52 \cdot T$	[18]
	$\Phi_{Cu}^{Ag} = -200898.33 - 56.23 \cdot T$	[4]
	$\Phi_{Cu}^{Cu,Ag} = 101042.71$	[4]
	$\Phi_{Cu}^{Ag,Mg} = -45687.66$	This work
Mobility of Mg	$\Phi_{Mg}^{Mg} = -112499 - 81.26 \cdot T$	[18]
	$\Phi_{Mg}^{Ag} = -200898.33 - 56.23 \cdot T$	[17]
	$\Phi_{Mg}^{Cu} = -170567 - 98.84 \cdot T$	[19]
	$\Phi_{Mg}^{Mg,Ag} = -308110.19 + 100.29 \cdot T$	[17]
	$\Phi_{Mg}^{Ag,Cu} = 98916.94$	This work

In order to verify the reliability of the obtained atomic mobility parameters, we compare the model-simulated composition profiles with the experimental values. Figure 2 presents the model-simulated composition profiles of solutes Cu and Mg for fcc Ag-Cu-Mg diffusion couples annealed at 1073 K for 24 h, in comparison with the measured ones denoted by symbols. As shown in this figure, the composition profiles simulated by the numerical

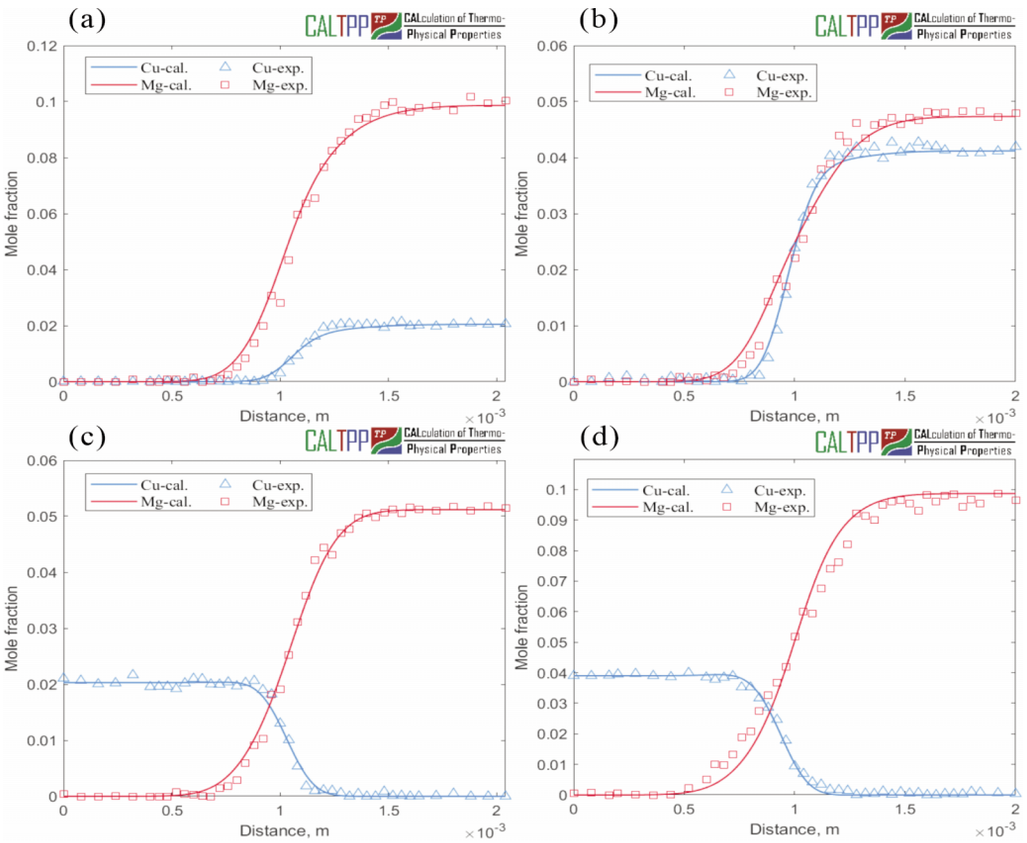

Figure 2. *Comparisons between the model-predicted composition profiles and measured ones for diffusion couples of (a) Ag/Ag−2.0Cu−9.8Mg, (b) Ag/Ag−4.1Cu−4.7Mg, (c) Ag−2.0Cu/Ag−5.1Mg and (d) Ag−3.9Cu/Ag−9.8Mg (at.%) annealed at 1073K for 24 hours*

inverse method agree well with the experimental ones, verifying the good reliability of the presently obtained mobilities.

Based on the available thermodynamic descriptions and the presently obtained atomic mobilities for fcc Ag-Cu-Mg phase, the three-dimensional surfaces for the interdiffusion coefficient at 1073 K are calculated, as shown in Fig. 3. It can be seen from the figure that the interdiffusion coefficient surfaces calculated by numerical inverse method are close to the symbols calculated by the Matano-Kirkaldy method. It can be also observed from Fig. 3 that all the interdiffusion coefficients increase with the increasing compositions of Cu and Mg.

According to the obtained surfaces of interdiffusion coefficients, the pre-exponential factor D_{0i} and the activation energies $Q_{ii}^{Ag}=(i=Cu \text{ or } Mg)$ are presented in terms of the Arrhenius equation[20]:

$$D_{ii}^{Ag}=D_{0i}\exp\left(\frac{Q_{ii}^{Ag}}{RT}\right) \quad (1)$$

Figures 4 and 5 present the composition-dependent D_{0i} and Q_{ii}^{Ag} (i = Cu, Mg), respectively. As seen in Fig. 4, D_{0Cu} decreases with the increasing composition of Cu, while D_{0Mg} decreases with the increasing composition of Mg. Both Q_{CuCu}^{Ag} and Q_{MgMg}^{Ag} decrease with the increasing composition of Cu and Mg, which can be concluded from Fig. 5.

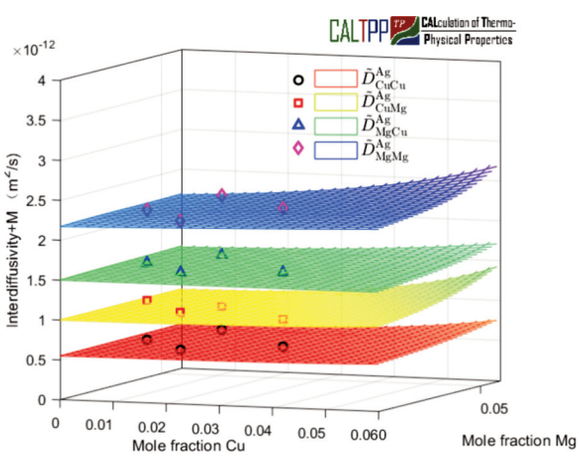

Figure 3. *Interdiffusion diffusion at 1073 K determined by the numerical inverse method (surfaces), compared with the results determined by Matano-Kirkaldy method (symbols)*

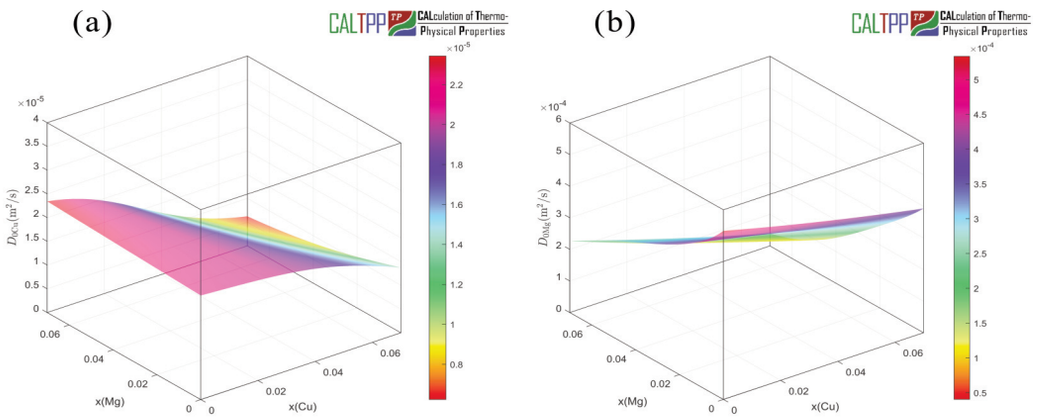

Figure 4. *Frequency factors in fcc Ag-Cu-Mg system (a) D_{0Cu} and (b) D_{0Mg}*

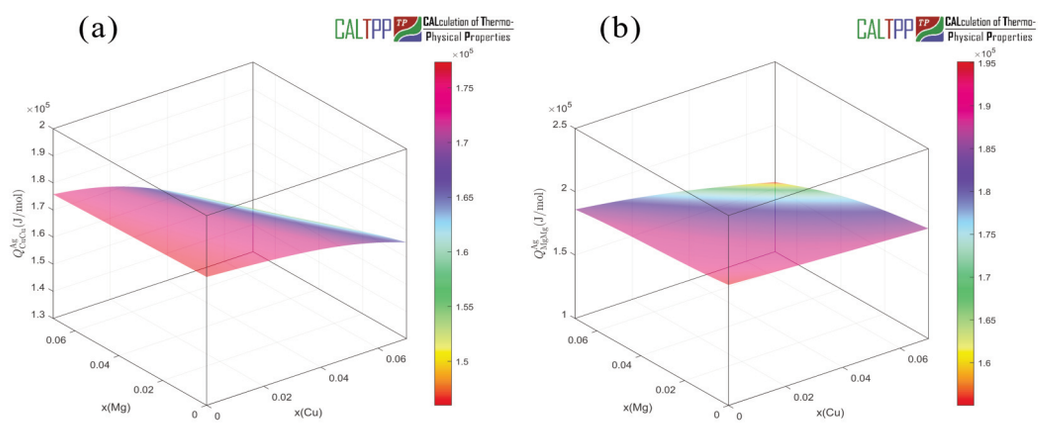

Figure 5. *Activation energies in fcc Ag-Cu-Mg system (a) Q^{Ag}_{CuCu} and (b)Q^{Ag}_{MgMg}*

4. Conclusions

In the present work, the diffusion coefficients and atomic mobilities for the fcc Ag-Cu-Mg phase were studied using the CALTPP program. The obtained atomic mobilities can reproduce well the measured composition profiles, and are thus very reliable. Moreover, the interdiffusion coefficient, activation energy, and pre-frequency factor along with the composition for the fcc Ag-Cu-Mg phase were predicted by the presently obtained atomic mobilities. The presently obtained atomic mobilities can be incorporated into the diffusion database for the Ag-based alloy, which can contribute to microstructure simulation and materials design.

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Authorship contribution statement

C.-B. Du: Experiments, Analysis, Writing − Original draft; S.-P. Huang: Methodology, Writing − Review & Editing; Q.-H. Min: Experiments, Methodology; Y.-L. Liu: Supervision, Analysis; S.-Y. Wen: Conceptualization, Writing − Review & Editing.

Data availability

Data available on request from the authors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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KOEFICIJENT INTERDIFUZIJE I POKRETLJIVOST ATOMA ZA FCC Ag-Cu-Mg FAZU NA TEMPERATURI OD 1073 K

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Apstrakt

U ovom radu, koeficijent interdifuzije i pokretljivost atoma za fcc Ag-Cu-Mg fazu na temperaturi od 1073 K su ispitivani kombinovanjem eksperimenata i proračuna difuzionih parova. Na osnovu eksperimentalnih profila sastava, metodom Matano-Kirkaldi izračunati su koeficijenti difuzije na presecima puteva difuzije. Koristeći termodinamičke opise dostupne u literaturi, pokretljivosti atoma za fcc Ag-Cu-Mg fazu su automatski optimizovane numeričkom inverznom metodom integrisanom sa programom CALTPP (CALculation of ThermoPhisical Properties). Štaviše, dobrim slaganjima između simuliranih i izmerenih profila sastava potvrđeno je da su dobijene vrednosti pokretljivosti atoma pouzdane. Pored toga, predstavljene su trodimenzionalne površine za koeficijent interdifuzije, energiju aktivacije i faktor frekvencije. Trenutno dobijene vrednosti pokretljivosti atoma mogu se inkorporirati u difuzionu bazu podataka za legure na bazi Ag, što može doprineti simulaciji mikrostrukture i dizajnu materijala.

Ključne reči: *Fcc Ag-Cu-Mg; Koeficijent interdifuzije; Mobilnost atoma; CALTPP; Energija aktivacije; Faktor frekvencije*