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Experimental and computational study of diffusion mobilities for fcc Ni–Cu–Mn alloys

Naqiong Zhu [a,b,c], Xiaojun Xu [a], Xiao-Gang Lu [a,b,c,d,*], Yanlin He [a,b,c], Jieyu Zhang [a,b,c], Hu Jiang [a]

[a] State Key Laboratory of Advanced Special Steel, Shanghai 200072, China
[b] Shanghai Key Laboratory of Advanced Ferrometallurgy, Shanghai 200072, China
[c] School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China
[d] Materials Genome Institute, Shanghai University, Shanghai 200444, China

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ABSTRACT

Based on the available thermodynamic description and experimental diffusivities, the diffusion mobilities of Ni, Cu and Mn for fcc Ni–Cu–Mn ternary alloys have been investigated in the present work. Interdiffusion coefficients for fcc Ni–Mn binary alloys with Mn content up to 60 at% and for Ni-rich fcc Ni–Cu–Mn ternary alloys were measured using diffusion couple method combined with Electron Probe Micro-Analyzer (EPMA) technique. During the assessment of diffusion mobilities by means of the CALPHAD method, experimental interdiffusivities for Cu-rich fcc Cu–Mn–Ni alloys were also taken into account. Comparisons between the results calculated using the diffusion mobilities assessed in the present work and the experimental data show that a good agreement has been obtained for the diffusion data such as the diffusion coefficients, concentration profiles and diffusion paths. Thus it is believed that the diffusion mobilities for fcc Ni–Cu–Mn alloys obtained in the present work can be applied for a wide composition range.

1. Introduction

Alloys containing Ni, Cu and Mn with various physical properties have found numerous applications in wide fields such as electronics and electrical industry [1], hydrometallurgy, chemical engineering and petroleum industry [2–4]. Moreover, the Ni–Cu–Mn alloy system is also of great interest for high-temperature shape memory alloys [5–9] and industrial damping alloys [10,11].

The diffusion simulation based on the thermodynamic description and the diffusion mobility permits prediction of almost all aspects of diffusion-controlled phenomena, such as diffusion coefficients, concentration profiles, microstructural stability and lattice plane displacement [12]. Since diffusion process greatly influences the microstructure and performance of alloys, knowledge of both thermodynamic and diffusion kinetic characteristics is of critical importance for designing and deploying advanced alloy systems. In this work, the diffusion mobility of the fcc phase is investigated for the Ni–Cu–Mn alloy system.

Sun et al. [13] performed the thermodynamic modeling for the Cu–Mn–Ni system and a self-consistent set of thermodynamic parameters were obtained. Based on Sun et al.'s work, Zhang et al. [14] optimized the diffusion mobility for Cu-rich fcc Cu–Mn–Ni alloys. By investigating the interdiffusion behavior in Ni-rich fcc Ni–Cu–Mn alloys, this work aims to obtain the diffusion mobility for fcc Ni–Cu–Mn alloys which can be applied for a wide composition range spanning from the Ni-rich corner to the Cu-rich corner. In addition, the fcc Ni–Cu, fcc Ni–Mn and fcc Cu–Mn binary systems were reassessed based on the new experimental data from the literature and this work.

In Zhang et al.'s work [14], the Ni self-diffusion mobility was directly taken from the work by Zhang et al. [15]. However, Campbell and Rukhin [16] evaluated the self-diffusion data of Ni using weighted means statistics and demonstrated that the analysis by Neumann and Tölle [17] agreed better with experimental data than the analysis by Jönsson et al. [18] and Zhang et al. [15]. In the present work, the Ni self-diffusivity determined by Neumann and Tölle [17] was adopted to reassess the diffusion mobility for the fcc Ni–Cu–Mn system by using the PARROT module incorporated in the DICTRA (DIffusion Controlled TRAnsformation) software [19].

* Corresponding author at: Materials Genome Institute, Shanghai University, Shanghai 200444, China.
E-mail address: xnew707@hotmail.com (X.-G. Lu).

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2. Evaluation of experimental diffusivities

The experimental diffusivities summarized and adopted in Zhang et al.'s work [14] were used in the present work. In addition, new experimental diffusivities for fcc Ni–Cu, Ni–Mn, Cu–Mn binary alloys and for fcc Ni–Cu–Mn ternary alloys were also adopted from the literature and measured in this work as summarized in Table 1. The new experimental diffusivities are briefly reviewed as follows.

2.1. The Ni–Cu system

All the critically reviewed diffusion coefficients for fcc Ni–Cu alloys given by Wang et al. [20] were used in the present assessment. Recently, Xu et al. [21] measured the interdiffusion coefficients for fcc Ni–Cu alloys from 1073 to 1273 K and reassessed the diffusion mobilities for the system by adopting the Ni self-diffusivity determined by Neumann and Tölle [17].

2.2. The Ni–Mn system

Using the diffusion couple method together with EPMA, interdiffusion coefficients for fcc Ni–Mn alloys with Mn content up to 60 at% were measured at 1223 and 1273 K in this work.

2.3. The Cu–Mn system

The fcc Cu–Mn system was assessed by Zhang et al. [14]. However, the interdiffusion coefficients calculated based on their diffusion mobilities deviate from the experimental data reported in Thibon et al.'s work [22], especially at low temperatures. Thibon et al. [22] studied the interdiffusion behavior in fcc Cu–Mn alloys using the diffusion couple technique in the temperature range from 723 to 1203 K. The concentration profiles were obtained by EPMA and the interdiffusion coefficients were determined from the diffusion profiles by the den Broeder's method [23] resulting from works of Sauer and Freise [24] and Wagner [25]. Whittenberger and Dayananda [26] measured the interdiffusion coefficients for fcc Cu–Mn alloys using Boltzmann–Matano method at 1123 K with Mn content up to 9 at%. Their values of interdiffusion coefficients agree with those obtained by Thibon et al. [22] at 1123 K.

2.4. The Ni–Cu–Mn system

Zhang et al. [14] adopted the interdiffusion coefficients measured for Cu-rich fcc Cu–Mn–Ni alloys by Takahashi et al. [27] during their optimization. In the present work, interdiffusivities for Ni-rich fcc Ni–Cu–Mn alloys at 1173 and 1373 K were investigated using diffusion couples and the concentration profiles were obtained by EPMA technique.

Table 1
Summary of new experimental diffusivities adopted and measured in this work.

System	Interdiffusion coefficient	Temperature (K)	Method	Refs.
Ni–Cu	$\widetilde{D}^{Ni}_{CuCu}$	1073–1272	Bulk diffusion couple method with EPMA technique	[20]
Ni–Mn	$\widetilde{D}^{Ni}_{MnMn}$	1223, 1273		This work
Cu–Mn	$\widetilde{D}^{Cu}_{MnMn}$	723–1203 1123		[21] [26]
Ni–Cu–Mn	$\widetilde{D}^{Ni}_{MnMn}$, $\widetilde{D}^{Ni}_{CuMn}$, $\widetilde{D}^{Ni}_{CuCu}$, $\widetilde{D}^{Ni}_{MnCu}$	1173, 1373		This work

Table 2
Diffusion couples and experimental conditions in this work.

No.	Nominal compositions of diffusion couples (at%)	Diffusion temperature (K)	Time (h)
NM1	Ni/Ni–60Mn	1273	24
NM2	Ni/Ni–60Mn	1223	36
A1	Ni–10Cu/Ni–20Mn	1373	12
A2		1173	72
B1	Ni–20Cu/Ni–20Mn	1373	12
B2		1173	72
C1	Ni–30Cu/Ni–30Mn	1373	12
C2		1173	72
D1	Ni–45Cu/Ni–30Mn	1373	12
D2		1173	72
E1	Ni–60Cu/Ni–30Mn	1373	12
E2		1173	72
F1	Ni/Ni–10Mn–55Cu	1373	12
F2		1173	72
G1	Ni/Ni–20Mn–36Cu	1373	12
G2		1173	72
H1	Ni/Ni–28Mn–10Cu	1373	12
H2		1173	72

3. Experimental procedures

Alloys and pure Ni blocks were prepared in an arc melting furnace in a high purity argon atmosphere. Raw materials were high-purity Ni (99.95 wt%), Cu (99.999 wt%) and Mn (99.95 wt%). The ingots were reversed and remelted five times. Then the ingots were annealed at 1373 K in sealed quartz tubes for 192 h before water-quenching to achieve homogeneity as well as to promote grain growth and decrease the effect of grain boundary diffusion. Bars with the size of $5 \times 5 \times 7$ mm^3 were cut by wire cutting. After being ground and polished, the alloys and pure Ni blocks were bound together with a specially-fabricated Mo clamp to assemble diffusion couples. The diffusion couple assemblies were again sealed in quartz tubes and annealed before water-quenching. The nominal compositions of diffusion couples and the experimental conditions are listed in Table 2. The concentration-distance profiles for diffusion couples were measured by EPMA on JEOL JXA 8100. In the end, the interdiffusion coefficients of binary and ternary systems were determined by Sauer–Freise [24] and Whittle–Green method [28], respectively.

4. Determination of the interdiffusion coefficients

The experimental concentration profiles of the diffusion couples were analyzed by the error function expansion (ERFEX) method as shown in the following equation [29,30],

$$X(\boldsymbol{z}) = \sum_i a_i erf\left(b_i \boldsymbol{z} - c_i\right) \tag{1}$$

where a_i, b_i and c_i are the fitting parameters, and z is the diffusion distance on diffusion couples. The parameters obtained from the ERFEX fitting reproduce the experimental data satisfactorily. The