CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 56 (2017) 230–240

Contents lists available at ScienceDirect

CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

journal homepage: www.elsevier.com/locate/calphad

Diffusion study in bcc_A2 Fe-Mn-Si system: Experimental measurement and CALPHAD assessment

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ARTICLE INFO

Keywords:
Bcc_A2 Fe-Mn-Si alloys
Diffusion
Interdiffusivity
Numerical inverse method
Atomic mobility

ABSTRACT

Based on the recently developed numerical inverse method, high-throughput measurement of the composition-dependent interdiffusivity matrices in the bcc_A2 Fe-Mn-Si alloys at 1173, 1273 and 1373 K was performed in the present work. To verify the reliability of the presently determined interdiffusivities, the ternary interdiffusivities evaluated by the traditional Matano-Kirkaldy method at the intersection points of the diffusion paths were employed to make a direct comparison. Subsequently, on the basis of the presently obtained interdiffusivities together with the thermodynamic descriptions for bcc_A2 phase in the Fe-Mn-Si system, atomic mobilities of Fe, Mn and Si in bcc_A2 Fe-Mn-Si alloys were assessed by means of DICTRA (DIffusion Controlled TRAnsformatim) software package. The comprehensive comparison between various calculated/model-predicted diffusion properties, including interdiffusivities, concentration profiles, interdiffusion fluxes and diffusion paths, and the experimental data indicates that most of the experimental data can be well produced by the presently obtained atomic mobilities. Moreover, the reliability of the present atomic mobilities was further validated by reproducing the experimental composition profiles which were not utilized in the assessment procedure.

1. Introduction

Due to the low cost and excellent machinability, Fe-based alloys are always attracting much attention. Mn and Si, which act as the main alloying components, are commonly added into the products of steel. Moreover, the additive of Si is often used as an equally strong ferrite (BCC) stabilizer in soft magnetic steels, electric steels and some oxidation-resistance steels for high-temperature applications [1]. A comprehensive understanding of both thermodynamic and kinetic characteristics is critical to quantitatively describe the microstructure evolution of the alloys during various materials process by using, i.e. the phase-field simulation [2,3]. Moreover, the knowledge of thermodynamics and kinetics in the Fe-Mn-Si system facilitates the understanding of the processes and applications of steels. During the past decades, several sets of thermodynamic descriptions in the Fe-Mn-Si system are available in the literature [4–7]. While in the kinetic aspect, the atomic mobilities in fcc_A1 phase of the Fe-Mn-Si system have been assessed by Zheng et al. [7] using the DICTRA (DIffusion-Controlled TRAnsformations) software package [8] based on their own experimental data and the literature data. As for bcc_A2 phase, only limited experimental diffusion coefficients over a narrow composition region were measured by Zhu et al. [9], and no reliable atomic mobility description exists in the literature.

To obtain reliable atomic mobility description for bcc_A2 Fe-Mn-Si system, abundant experimental diffusivity information over the wide composition range is highly needed. For a ternary system, the solid diffusion couple technique together with the traditional Matano-Kirkaldy method and/or its variants is the most widely used approach to retrieve the experimental interdiffusion coefficients [10–12], but this traditional approach is considered to be of low efficiency. That is because only the interdiffusivity matrices at the intersection points along the diffusion paths of every two well-designed ternary diffusion couples can be obtained. In order to circumvent the situation, a so-called pragmatic numerical inverse method has been recently developed in our research group [13], and can provide high-throughput measurements of the interdiffusion coefficients based on the single diffusion couple. The main idea of such method is to iteratively adjust the parameters and then obtain least error between the experimental and the simulated composition profiles. The experimental composition profiles are measured from the diffusion couple experiments and the simulated composition profiles are generally produced by solving the Fick's second law. This numerical inverse method has been successfully

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http://dx.doi.org/10.1016/j.calphad.2017.01.008
Received 17 November 2016; Received in revised form 16 January 2017; Accepted 29 January 2017

applied in several ternary systems later [14,15]. Very recently, this method has been augmented, and can be applicable in alloy systems ranging from binary to multicomponent alloys [16].

Consequently, the diffusion couple technique together with the numerical inverse method [13,16] is to be employed to perform the high-throughput measurement of the composition-dependent interdiffusivities in bcc_A2 Fe-Mn-Si alloys, from which the atomic mobility descriptions of bcc_A2 phase in the ternary Fe-Mn-Si system can be then assessed. The major targets of the present work are: (*i*) to determine the composition-dependent interdiffusivities of bcc_A2 Fe-Mn-Si alloys at 1173 K, 1273 K and 1373 K by using both numerical inverse method and traditional Matano-Kirkaldy method in combination with diffusion couple technique; (*ii*) to evaluate the atomic mobilities of bcc_A2 phase in the Fe-Mn-Si system based on the experimental diffusivities from the present work and the literature; (*iii*) to verify the presently obtained atomic mobilities by comprehensively comparing various calculated/simulated diffusion properties with the corresponding experimental data, including interdiffusivities, concentration profiles, interdiffusion fluxes, and diffusion paths.

2. Experimental procedure

Iron (purity: 99.99 wt%), manganese (purity: 99.9 wt%), and silicon (purity: 99.999 wt%) were used as starting materials. Six diffusion couples were prepared as shown in Table 1 according to the following steps. Firstly, different amounts of pure Fe, Mn, and Si corresponding to the terminal compositions were melted by arc melting under Ar atmosphere using a non-reactive W electrode (WKDHL-1, Opto-electronics Co., Ltd., Beijing, China) for four times to improve their homogeneity. It should be mentioned that Mn has a high vapor pressure [17], and Mn was stacked between Fe and Si to minimize evaporation. Nevertheless, weight loss still exists during arc melting. By assuming that all the loss was caused by the evaporation of Mn, an additional gram of Mn was added per ingot to compensate for its evaporation in order for its location in bcc_A2 single-phase region. Subsequently, the samples were linearly cut into suitably sized blocks ($4\times3\times8$ mm^3) after mechanically removing the surface materials, and then sealed into evacuated quartz tubes, homogenized at 1373 ± 5 k for 10 days in an L4514-type diffusion furnace (Qingdao Instrument & Equipment Co., Ltd., China), followed by quenching in cold water. After that, all the samples were grounded on SiC paper to remove surface contamination and were then bound together with Mo clamps to form diffusion couple as shown in Table 1. The diffusion assemblies were then sealed into evacuated quartz tubes, and annealed at certain temperatures and times, as listed in Table 1, in an L4514-type diffusion furnace, followed by quenching in cold water. After standard metallographic techniques, the concentration profiles of each couple were measured by means of EPMA technique (JXA-8230, JEOL, Japan). The error for concentration measurements is within 1%.

Table 1
List of terminal compositions for the six diffusion couples in the present work.

Couple No.	Composition (at%)	Diffusion temperature (K)	Diffusion time (h)
C1	Fe-0.2Mn-20.0Si/Fe--3.7Mn-13.4Si	1173	48
C2	Fe-10.0Mn-19.7Si/Fe-15.1Si	1173	48
C3	Fe-15.1Si/Fe-10.0Mn-19.4Si	1273	25
C4	Fe-3.6Mn-13.5Si/Fe-0.3Mn-20.2Si	1273	25
C5	Fe-0.3Mn-20.1Si/Fe-3.5Mn-13.3Si	1373	15
C6	Fe-10.2Mn-19.8Si/Fe-15.3Si	1373	15

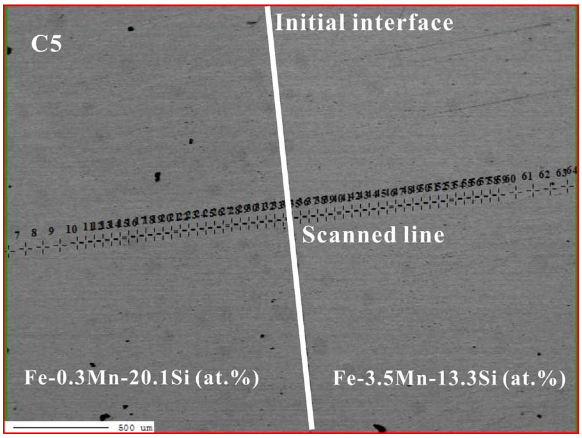

Fig. 1. Backscatter electron image of the C5 (Fe-0.3Mn-20.1Si/Fe-3.5Mn-13.3Si) diffusion couple annealed at 1373 K for 15 h.

3. Methodology

3.1. Numerical inverse method

Following Manning's random alloy model [18], the interdiffusivities $\widetilde{D}_{ij}^{3}(i, j=1 \text{ or } 2)$ in a fictitious ternary 1–2–3 system (here, 1 and 2 are solutes while 3 is solvent) and the mobility M_i are related by [13,16].

$$\widetilde{D}_{ij}^{3} = RT\left[M_i\varphi_{ij}^{3} - c_i(\mathrm{M}_1\varphi_{1\mathrm{j}}^{3} + M\varphi_{2j}^{3} + M\varphi_{3j}^{3}\right]$$
$$+s\left[(M_i - c_1M_1 - c_2M_2 - c_3M_3)\frac{2c_iRT\sum_m(M_m\varphi_{mj}^{3})}{A_0\sum_m c_mM_m}\right] \quad (1)$$

where R is the gas constant and T is the temperature. φ_{ij}^{3} is the thermodynamic factor, and can be obtained from the corresponding thermodynamic descriptions, which are usually available for most alloy systems nowadays.

$$\varphi_{\mathrm{ij}}^{3} = \frac{c_i}{RT}\left(\frac{\partial\mu_i}{\partial c_j} - \frac{\partial\mu_i}{\partial c_3}\right) \quad (2)$$

The second part on the right side of Eq. (1) denotes the vacancy-wind effect, which considers the contribution of the vacancy flux. When the vacancy-wind effect is considered, s equals to 1, otherwise, s equals to 0. The parameter A_0 is a factor depending only on crystal structure, and here equals to 5.33 for bcc crystals [18]. The function developed by Andersson and Ågren [8] and incorporated in DICTRA software [19] was employed in the present work to express the atomic mobility for element i:

$$M_i = \frac{1}{RT}\exp\left(\frac{\Delta\phi_i}{RT}\right) \quad (3)$$

where $\Delta\phi_i$ can be expanded by the Redlich-Kister polynomial:

$$\Delta\phi_i = c_1\Delta\phi_i^{1} + c_2\Delta\phi_i^{2} + c_3\Delta\phi_i^{3} + c_1c_2\Delta\phi_i^{1,2} + c_1c_3\Delta\phi_i^{1,3} + c_2c_3\Delta\phi_i^{2,3}$$
$$+ c_1c_2c_3\Delta\phi_i^{1,2,3} \quad (4)$$

Here,$\Delta\phi_i^{1}$,$\Delta\phi_i^{2}$ and $\Delta\phi_i^{3}$ are the end-members for diffusion element i in elements 1, 2 and 3, while $\Delta\phi_i^{1,2}$, $\Delta\phi_i^{1,3}$, $\Delta\phi_i^{2,3}$ and $\Delta\phi_i^{1,2,3}$ are the interaction parameters for the mobility of element i in the 1–2, 1–3, 2–3 and 1–2-3 system, respectively. For simplicity, $\Delta\phi_i^{1}$, $\Delta\phi_i^{2}$ and $\Delta\phi_i^{3}$ are usually available according to self- and impurity diffusivities, which can be easily obtained from the experimental data, first-principle calculations, molecular dynamic simulation or some semi-empirical relations. The other parameters, including $\Delta\phi_i^{1,2}$, $\Delta\phi_i^{1,3}$, $\Delta\phi_i^{2,3}$ and $\Delta\phi_i^{1,2,3}$, are usually considered as adjustable parameters. In most cases, one or two of them are needed to be evaluated for one diffusion couple.

When an estimation of the adjustable parameters is provided, the