CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry 49 (2015) 58–66

Contents lists available at ScienceDirect

CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

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

Diffusivities in liquid and fcc Al–Mg–Si alloys and their application to the simulation of solidification and dissolution processes

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ARTICLE INFO

Article history:
Received 18 January 2015
Received in revised form
18 March 2015
Accepted 19 March 2015
Available online 23 March 2015

Keywords:
Al–Mg–Si alloys
Atomic mobility
Diffusivity
Viscosity
Solidification

ABSTRACT

The experimental viscosities and diffusivities in Al–Mg–Si melts as well as the experimental diffusivities in fcc Al–Mg–Si alloys available in the literature were first critically reviewed. The Sutherland equation was then employed to convert the experimental viscosity data into self-/tracer diffusivity data in Al–Mg–Si melts. Based on the experimental diffusivities together with the converted ones, the atomic mobilities in liquid and fcc phases of the Al–Mg–Si system were assessed by means of DIffusion-Controlled TRAnsformation (DICTRA) software package. Comprehensive comparisons showed that most of the measured and converted diffusivities in liquid and fcc Al–Mg–Si system can be reasonably reproduced by the currently obtained atomic mobilities. Moreover, the reliability of the established atomic mobilities of liquid and solid phases were further verified by two typical cases in Al–Mg–Si alloys during solidification and dissolution processes. The simulation results agree well with the experimental information, not only validating the reliability of the atomic mobilities, but also demonstrating the importance of the accurate atomic mobility database in quantitative simulation of microstructure during various preparation processes.

1. Introduction

Mg and Si are two common elements of casting and wrought aluminum alloys. Al–Mg–Si based 6 × × × Al alloys are widely utilized in automotive construction and the aerospace industries [1–4] due to high strength-to-density ratio, functional extrudability, age hardening characteristics, excellent corrosion resistance, and surface and welding properties. Alloy performance is highly dependent on microstructure formation during the preparation process [5,6]. Improvements in alloy performance require quantitative description and accurate control of microstructure evolution in the target alloy during the preparation process.

Recent research indicates that quantitative phase-field simulation is a feasible method to achieve this goal [7–9]. CALculation of PHAse Diagram (CALPHAD) thermodynamic and atomic mobility databases [10–12] are the prerequisite for quantitative phase-field simulation [13–15]. Reliable thermodynamic databases for a wide variety of alloys have been constructed [10,11] for the past 30 years utilizing CALPHAD approach; however, atomic mobility databases have not developed similarly. Several sets of thermodynamic descriptions [16–19] exist for the technically significant Al–Mg–Si system for example, but atomic mobility databases are not available.

A major obstacle associated with the establishment of atomic mobilities in both solid and liquid phases of the Al–Mg–Si system is the lack of adequate diffusion coefficients, especially for the liquid phase due to experimental difficulties caused by convection in melts. Zhang et al. [20] assessed atomic mobilities for the liquid phase based on both experimental and theoretically predicted diffusion coefficients via the DIffusion-Controlled TRAnsformation (DICTRA) software package. A preliminary atomic mobility database for liquid phase in multicomponent Al alloys has been successfully established with this strategy [21]. Experimental and theoretical diffusivities, usually limited in the research for most alloys; however, are still relied upon by this strategy. Research also reviewed recent work by Chen et al. [22], who modified the Sutherland equation to establish the correlation between diffusivity and viscosity. Considering the limited viscosity data, the Kozlov model was chosen for representing viscosities in binary and multicomponent melts, allowing predictions of different diffusivities in the target alloys and development of an atomic mobility database for melts. The fit degree of the predicted viscosities by the chosen Kozlov model to the experimental data is the key factor determining the reliability of the estimated diffusivities.

The Sutherland equation [23] is a more efficient application for systems with large viscosity data sets, such as the Al–Mg–Si system, as viscosity data is converted into the tracer diffusivity data in melts, from which the atomic mobility database for liquid phase can be then established. The main objectives of this study are: i) to critically review research for all measured diffusivities and

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http://dx.doi.org/10.1016/j.calphad.2015.03.002
0364-5916/

viscosities in unary, sub-binary and ternary melts of the Al–Mg–Si system and diffusivities in fcc Al–Mg–Si alloys; ii) to convert viscosity data into self-diffusivities in sub-unary melts and to convert tracer diffusivities in sub-binary and ternary melts; iii) to evaluate atomic mobilities in liquid and fcc phases of the Al–Mg–Si system utilizing the DICTRA software package; iv) to verify reliability of the established atomic mobilities of liquid and solid phases by choosing two typical cases in Al–Mg–Si alloys during solidification and dissolution processes, and to demonstrate significance of the accurate atomic mobility database for liquid phase in quantitative simulation of microstructure during solidification.

2. Model description

2.1. Sutherland equation

Sutherland [23] derived a diffusion equation based on Stokes Law which relates diffusivity to viscosity of the liquid metal:

$$D = \frac{kT}{6\pi\eta r}\left(\frac{1 + 3\eta/\beta r}{1 + 2\eta/\beta r}\right) \tag{1}$$

where k is the Boltzmann constant, r is radius of the diffusing unit, η is viscosity in the melts, and β is the coefficient of sliding friction between the diffusing particle and the medium. Solute atoms movement among solvent atoms of equal size, in one extreme case, reveal solute atoms expediently traveling between gaps of the solvent atoms and, in this case, β is equal to 0. The Sutherland equation for the self-diffusivity of a pure liquid metal A, $D_{\mathrm{A}}^{\mathrm{self}}$ then may be written as:

$$D_{\mathrm{A}}^{\mathrm{self}} = \frac{kT}{4\pi\eta_A r_A} \tag{2}$$

The tracer diffusivities of A, D_{A}^{*}, in a A–B alloy based on the Sutherland equation may be expressed as:

$$D_{\mathrm{A}}^{*} = \frac{kT}{6\pi\eta r_A}\left(\frac{1 + 3\eta/\beta_{AB} r_B}{1 + 2\eta/\beta_{AB} r_B}\right) \tag{3}$$

Chen et al. [22] recently suggested, if $T_A^m < T_B^m$ or $r_A/r_B \le 1.01$ when $T_A^m \ge T_B^m$, β_{AB} is equal to 0. 0.01 is introduced to allow a small difference for the radius of the solute A and solvent B atoms. Eq. (3) may then be simplified to be:

$$D_{\mathrm{A}}^{*} = \frac{kT}{4\pi\eta r_A} \tag{4}$$

If $r_A/r_B > 1.01$ when $T_A^m \ge T_B^m$, β_{AB} approaches to infinite,thus, Eq. (3) may be re-written as:

$$D_{\mathrm{A}}^{*} = \frac{kT}{6\pi\eta r_A} \tag{5}$$

More precise temperature-dependent diffusivities in melts may be obtained by the following temperature-dependent radius [24]:

$$r_i(T) = \left\{\frac{3f\cdot V_i^m\cdot[1 + \alpha_i\cdot(T - T_i^m)]}{4\pi N_A}\right\}^{1/3} \tag{6}$$

where f is the volume-packing which approaches to 0.45, V_i^m is the molar volume of element i at melting temperature T_i^m, α_i is the thermal expansion coefficient of pure element i, and N_A is the Avogadro number.

2.2. Atomic mobility

The Arrhenius equation is typically employed to describe self-diffusion and impurity diffusion in liquids where the identity of the activation energy is uncertain [25], though the mechanism of diffusion in liquids varies from that in solids. The Darken equation is also widely applied to estimate the inter-diffusion coefficients in simple liquids [26]. Equations applied in these circumstances suggest the concept of atomic mobility and the model for multi-component diffusionin simple phases introduced by Anderson and Ågren [27] may also be applied to the liquid phase. Recent related research from our research group successfully demonstrated the application of atomic mobility concepts in simple liquid phase of both multicomponent Al and solder alloys [20–22], thus, the model developed by Anderson and Ågren [27] is also employed to investigate diffusion in Al–Mg–Si melts in the present work. The operating diffusion mechanism is not identified as only phenomenological treatment of various diffusion coefficients in liquid is performed.

According to Andersson and Ågren [27], the atomic mobility (M_B) for an element B in both liquid and fcc phases can be expressed as:

$$M_B = \exp\left(\frac{\Phi_B}{RT}\right)\frac{1}{RT} \tag{7}$$

where R is the gas constant, T the temperature, while $\Phi_B = -Q_B + RT\ \ln M_B^0$, with Q_B as the activation enthalpy and M_B^0 as a frequency factor. Φ_B is generally dependent on the composition, temperature and pressure. Similar to the CALPHAD approach [28], the composition dependency of Φ_B can be represented by a linear combination of the values at each endpoint of the composition space in a Redlich–Kister expansion:

$$\begin{aligned}\Phi_B = {} & \sum_i x_i\,\Phi_B^i + \sum_i \sum_{j>i} x_i x_j \left[\sum_{r=0}^{m} {}^r\Phi_B^{i,j}(x_i - x_j)^r\right] \\ & + \sum_i \sum_{j>i} \sum_{k>j} x_i x_j x_k \left[\sum_{s=0} v_{ijk}^s\,{}^s\Phi_B^{i,j,k}\right] \quad (s \\ = {} & i, j, k)\end{aligned} \tag{8}$$

where x_i is the mole fraction of element i, Φ_B^i is the value of Φ_B for pure i, ${}^r\Phi_B^{i,j}$ are binary interaction parameters and ${}^s\Phi_B^{i,j,k}$ are ternary parameters. The parameter v_{ijk}^s is derived by an equation in the form:

$$v_{ijk}^s = x_s + (1 - x_i - x_j - x_k)/3 \tag{9}$$

With atomic motilities known, the tracer diffusion coefficient (D_i^*) is then related to the atomic mobility via a simple relation, $D_i^* = RTM_i$. The inter-diffusion coefficient (D_{kj}^n), which relates the flux of element k with the gradient of component j and reference component n, is derived by:

$$D_{kj}^n = \sum_i (\delta_{ik} - x_k)x_i M_i \left(\frac{\partial u_i}{\partial x_j} - \frac{\partial u_i}{\partial x_n}\right) \tag{10}$$

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

3. Literature review

All critically reviewed experimental diffusivities and viscosities in liquid Al–Mg–Si alloys and the experimental diffusivities in fcc Al–Mg–Si alloys available in the literature are summarized in Table 1 and briefly categorized in the following.

3.1. Diffusivities

Reported experimental diffusivities associated with Al–Mg–Si melts are limited. Demmel et al. [29] and Kargl et al. [30] recently