Diffusion Kinetics in Crystals

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The University of Newcastle, Australia
Faculty of Engineering and Built Environment
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Declarations

Statement of Originality

I hereby certify that the thesis contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. I give consent to this copy of my thesis when deposited in the University Library, being made available for loan and photocopying subject to the provisions of the Copyright Act 1968.

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This is to certify that the thesis is submitted in the form of a series of published papers of which I am a joint author. I have included as a part of the thesis a written statement from each co-author, and endorsed by the Faculty Assistant Dean (Research Training), attesting to my contribution to the joint publications.

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Tumpa Rani Paul

Statement of Contribution

A written statement has been obtained from the following co-authors attesting my contribution to joint publications included as part of this thesis. Statements summarising and clearly identifying the nature and extent of the intellectual input by myself are included as part of the thesis.

Professor Graeme E. Murch

Professor Irina V. Belova

Professor Alan R. Allnatt

Dr Alexander V. Evteev

Dr Elena V. Levchenko

Dedication

To my parents

They always inspire me at every step in my life.

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Table of Contents

List of Publications and Awards

List of publications included as part of this thesis

This thesis is based on the following peer reviewed scientific published papers, listed in the following sequence within the present manuscript.

1. **T. R. Paul**, I. V. Belova, E. V. Levchenko, A. V. Evteev and G. E. Murch, "Determining a Tracer Diffusivity by way of the Darken-Manning Equation for Interdiffusion in Binary Alloy Systems", *Diffusion Foundations*, vol. 4, pp. 25-54, 2015.

2. **T. R. Paul**, I. V. Belova and G. E. Murch, "Random alloy diffusion kinetics for the application to multicomponent alloy systems", *Philosophical Magazine*, vol. 96, pp. 1228-1244, 2016.

3. A. R. Allnatt, **T. R. Paul**, I. V. Belova and G. E. Murch, "A high accuracy diffusion kinetics formalism for random multicomponent alloys: application to high entropy alloys", *Philosophical Magazine*, vol. 96, pp. 2969-2985, 2016.

4. **T. R. Paul**, I. V. Belova and G. E. Murch, "Analysis of Diffusion in High Entropy Alloys", *Materials Chemistry and Physics*, 2017. https://doi.org/10.1016/j.matchemphys.2017.06.039

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Conference presentations

- I. V. Belova, **T. R. Paul** and G. E. Murch, "Access to One Tracer Diffusivity from the Interdiffusivity and the Other Tracer Diffusivity in a Binary Alloy", Materials Science & Technology Conference and Exhibition (MS&T) October 4-8, 2015, Columbus, USA.

- **T. R. Paul**, I. V. Belova and G. E. Murch, "Random Alloy Kinetics Theory for Analysing Tracer Diffusion and Interdiffusion in Binary Alloy Systems", 12th International Conference on Diffusion in Solids and Liquids (DSL) June 26-30, 2016, Split, Croatia.

- **T. R. Paul**, I. V. Belova and G. E. Murch, "Application of Random Walk Diffusion Theories to the High Entropy Alloys", 9th International Conference on Materials for Advanced Technologies (ICMAT) June 18-23, 2017, Suntec, Singapore.

Awards

- Postgraduate Research Poster Competition Prize, Mechanical Engineering, Faculty of Engineering and Built Environment, University of Newcastle, Australia, 2016.

List of Symbols

Arabic Symbols	
Symbol	**Description**
a	Lattice parameter
a_i	Thermodynamic activity
A^*	Isotope of A atom
c_i	Composition (atomic fraction)
c_V	Vacancy fraction
D	Diffusion coefficient or diffusivity
D_0	Pre-exponential factor
${D_i}^*$	Tracer diffusion coefficient of atoms i
${D_i}^{*(0)}$	Uncorrelated part of tracer diffusion coefficient
D_i^{exp}	Experimentally obtained self-diffusion coefficients of species i
D_i^I	Intrinsic diffusion coefficient of species i
$\widetilde{D}$	Interdiffusion or chemical diffusion coefficient
f_0	Geometric correlation factor
f_i	Tracer correlation factor of species i
f_{ii}	Diagonal collective correlation factors
${f_{ij}}^i$	Off-diagonal collective correlation factors
h	External/magnetic field
H	Energy
H_i	Vacancy escape frequency of species i
$\langle ij \rangle$	Sum of all nearest neighbouring pairs of spins
J_i	Flux of species i in the crystal lattice reference frame
J_i^0	Flux of species i in the laboratory reference frame
k	Boltzmann constant
L_{ij}	Onsager phenomenological coefficients or transport coefficients
${L_{ii}}^{(o)}$	Uncorrelated part of diagonal phenomenological coefficients
M_0	Parameter directly related to the geometrical correlation factor f_0
n	Number of atomic species

n_i, N_i	Total number of jumps of species i
N	Number of lattice sites per unit volume
p_V	Vacancy availability factor
P	Pressure
Q	Activation energy
r	Jump distance
${\Delta r_i}^2$	Mean-square displacement of an atom i
$\boldsymbol{R}$	Vector position of all atoms of species i
$\Delta \boldsymbol{R}_i$	Vector displacement of all atoms of species i
s_i	Spin of species i
S	Vacancy-wind factor
t	Time
T	Absolute temperature
T_c	Critical temperature
v	Velocity of lattice reference frame relative to the laboratory reference frame
V	Volume, Ordering energy
V_{ij}	Nearest-neighbour interaction energy
w_i	Atom-vacancy exchange frequency of atomic species i, jump frequency
x_k	Kirkendall shift in the x direction
X_i	Driving forces of species i
X_V	Effective forces acting on vacancies

Greek Symbols	
Symbol	**Description**
γ_i	Activity coefficient of species i
Γ_i	Jump rate of atomic component i
δ_{ij}	Kronecker delta
λ	Jump distance
μ_i	Chemical potential of species i
φ	Thermodynamic factor
Ψ	Time correlation functions

Abbreviations	
Abbreviation	**Description**
2D	Two dimensional
bcc	Body-centred cubic
CWM	Correlated Walk Model
fcc	Face-centred cubic
HE	Holdsworth and Elliott
HEA	High Entropy Alloy
KMC	Kinetic Monte Carlo
MAA	Moleko, Allnatt and Allnatt
MC	Monte Carlo
sc	Simple cubic
SIMS	Secondary Ion Mass Spectrometry

Abstract

In this study, the full diffusion kinetics behaviour for phenomenological coefficients, interdiffusion coefficients and tracer diffusion coefficients of atomic components in crystalline solids is investigated. The main theoretical approach for this investigation is the hierarchy of random alloy approximations. The combined analysis of tracer or self-diffusion coefficients with the interdiffusion coefficient is also performed. The basic information on the interrelation of the tracer and collective diffusion processes is provided by the chosen theory of diffusion kinetics. Furthermore, extensive Kinetic Monte Carlo (KMC) simulation results are used for the testing and development of analytical diffusion kinetics approaches for binary and multicomponent alloy systems.

As part of the present research, the solution to a problem that is often encountered in the experimental investigation on the self- and interdiffusion coefficients is considered. Namely, in the case of a binary alloy it is often necessary (via the Darken-Manning equation) to find the tracer diffusion coefficient where the other tracer diffusion coefficient and interdiffusion coefficient are available. Several numerical tests are performed to examine the solution and compared them with the available experimental data.

Further, in this study, the diffusion kinetics formalisms of Darken, Manning, Holdsworth and Elliott (HE), and Moleko, Allnatt and Allnatt (MAA) are analysed in detail. These formalisms are then extended and applied for the cases of multicomponent random alloy models. Moreover, a new version of the highly accurate MAA theory, called MAA-light, is developed for describing diffusion kinetics in multicomponent random alloys. In addition, the resulting expressions from the approaches are verified by means of KMC simulation and the possible range of the tracer diffusion coefficient ratio of the highest atomic mobility to the lowest atomic mobility is analysed. It is shown that the overall results for the theories are in reasonably good agreement with the simulation results. An iterative method for the case of the multicomponent system is also developed to find the uncorrelated parts of the tracer diffusion coefficients and tracer correlation factors with reasonable accuracy. In this research, the diffusion kinetics theory is focused on a special type of

multicomponent alloy, namely, high entropy alloys (HEAs). The self-diffusion and interdiffusion kinetics are investigated by extending and applying three diffusion kinetics approaches in the case of face centred cubic high entropy alloy $CoCrFeMn_{0.5}Ni$.