# Atomic-scale modeling of twinning in titanium and other HCP alloys

Dissertation

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

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2019

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2019

#### Abstract

Titanium (Ti) and its alloys have a wide range of applications in biomedical, automotive and aerospace industries due to their excellent strength to weight ratio and corrosion resistance. Alpha phase Ti has hexagonal closed packed (hcp) structure that shows anisotropic plastic deformation;  $\langle a \rangle$  type slip on prism planes is the easiest to activate but cannot accommodate deformation along the  $\langle c \rangle$  axis. The low temperature ductility of Ti is linked to twinning. Therefore, understanding the mechanisms behind the twin nucleation and growth in Ti alloys is important from both theoretical and industrial application points of view. To that end, the present study seeks a better understanding of the atomic scale processes involved in twin nucleation mechanisms and the effect of alpha-stabilizing solutes such as interstitial oxygen, substitutional aluminum and rare earth elements on twinning. Systematic molecular dynamics (MD) simulations are used to identify the underlying mechanism of twin nucleation from dislocation/grain boundary interactions. Density functional theory (DFT) simulations are employed to examine the effect of oxygen interstitials on the twinning behavior of Ti. A systematic framework has been developed to predict the diffusion of interstitial elements near the twin boundaries in hcp alloys. Next, uncertainty that arises from first-principles calculations in predicting diffusion coefficients are quantified. Finally, solute segregation to the twin boundaries as a new mechanism for dynamic strain aging (DSA) is investigated in Ti and other hcp alloys.

To Love...

#### Acknowledgments

I would be nowhere close to where I am without the help of many people. Most immediately, I express my sincerest and deepest thanks to my advisor Dr. Maryam Ghazisaeidi. I am grateful to Maryam for her devoted guidance and continuous support. She has been a wonderful mentor who cared about me and my work and directed me in the right track. She constantly gave me courage through all inevitable ups and downs in my research work and taught me how to critically look into problems. Maryam, it has been a great privilege for me to be your student and work under your supervision; Thanks for everything!

I am very grateful to several other professors for their insightful comments and discussions. Special thanks to Dr. Wolfgang Windl, who was on both my Candidacy and Dissertation committees, and who always provided me with helpful suggestions and has been very supportive throughout my studies. I am very thankful to Dr. Michael Mills, who was on both my Candidacy and Dissertation Committees, and whose theoretical insights on microstructure and mechanical properties of materials and experimental approaches broadened my view on investigating the deformation mechanisms at the atomic-scales. I would also like to acknowledge fruitful discussions and collaboration with Dr. Ji-Cheng Zhao.

Because of Dr. Ghazisaeidi's acknowledged excellence in the field, I had several valuable opportunities to collaborate and discuss my research with other professors outside of Ohio State University. I am very glad and thankful for having met and collaborated with Dr. Dallas Trinkle at University of Illinois, Urbana-Champaign from whom I learned many novel methods and concepts on diffusion calculations. I am also thankful to Dr. William Curtin for being generous with his time and kindly giving me constructive feedback in our conversations during conferences.

I am deeply thankful to my parents, Behnaz and Behrouz, for their kind support and sacrifices throughout all these years. They have been always motivating me to continue my education to the highest academic levels and without their guidance, I could have never dreamed of the opportunities available for me today. I am also thankful to my sister, Sara, for her unconditional love. I am greatly indebted to my grandma and my first teacher whose pure love, support and kindness have been and will be with me in my heart.

I extend my special thanks to the current and former members of the Ghazisaeidi Group: Dr. Daniel Buey, Dr. Changning Niu, You Rao, Carlyn LaRosa, Mulaine Shih, Sevim Polat Genlik, Julian Brodie and Dr. Edwin Antillon. These thanks also extend to the great colleagues who I have had the opportunity to collaborate with. In particular, Dr. Timothy Smith, Dr. Jiashi Miao, Dr. Babu Viswanathan, and Dr. Wei Zhong. I also acknowledge Dr. Connor Slone, Dr. Christian Oberdorfer, John Jamison and Dr. Alex Brust for their faithful friendship and insightful discussions.

Special thanks to my best friend and roommate, Mamzi Bayatpur, for our nine-years of friendship and for all enjoyable times we have shared together which made my academic journey enjoyable. I also thank my friends who I have been always consulting with in the past. In particular, I need to thank Dr. Morteza Hashemi, Dr. Ali Tehranchi, Dr. Pezhman Arab, Dr. Farzaneh Ojaghnezhad, and Nima Mirzaei.

Finally, I would like to thank the U.S. Department of Energy, Office of Science, Basic Energy Sciences for funding this research through the grant number DE-SC0012481 and

the support I received from the dedicated staff at the Ohio Supercomputer Center, without whom the computations in this project would never have been possible.

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- 1. **M.S. Hooshmand**, M. Ghazisaeidi, "Solute/Twin boundary interaction as a new atomic-scale mechanism for Dynamic Strain Aging: I. Interstitial diffusion", (*ready for submission*)
- 2. **M.S. Hooshmand**, M. Ghazisaeidi, "Solute/Twin boundary interaction as a new atomic-scale mechanism for Dynamic Strain Aging: II. Vacancy-mediated diffusion ", *(in preparation)*
- 3. **M.S. Hooshmand**, G. Viswanathan, M.J. Mills, M. Ghazisaeidi, "Slip induced twinning in Titanium", (*in preparation*)

- 4. W. Zhong, **M.S. Hooshmand**, M. Ghazisaeidi, W. Windl, JC. Zhao, "A comprehensive experimental and computational study of the diffusion and mobility of the Al-Mg binary system", (*under review*)
- M.S. Hooshmand, C. Niu, D.R. Trinkle, M. Ghazisaeidi, "First-principles prediction of oxygen diffusivity near the (1012) twin boundary in Titanium", *Acta Materialia* (2018) (link)
- T.M. Smith, B.D. Esser, B. Good, M.S. Hooshmand, G.B. Viswanathan, C.M.F. Rae, M. Ghazisaeidi, D.W. McComb, M.J. Mills, "Segregation and phase transformations along superlattice intrinsic stacking faults in Ni-based superalloys", *Metallurgical and Materials Transactions A*, (2018),1-13 (link)
- 7. **M.S. Hooshmand**, M.J. Mills, M. Ghazisaeidi, "Atomistic modeling of dislocation interactions with twin boundaries in Ti", *Modelling and Simulation in Materials Science and Engineering (2017)* (link)
- T.M. Smith, B.D. Esser, M.S. Hooshmand, E.P. George, F. Otto, M. Ghazisaeidi, D.W. McComb, M.J. Mills, "Through-Focal HAADF-STEM Analysis of Dislocation Cores in a High-Entropy Alloy", *Microscopy and Microanalysis, Vol.* 22 (2016) (link)
- T.M. Smith, M.S. Hooshmand, B.D. Esser, F. Otto, D.W. McComb, E.P. George, M. Ghazisaeidi, M.J. Mills, "Atomic-scale characterization and modeling of 60° dislocations in a high-entropy alloy", *Acta Materialia, Vol. 110* (2016) (link)

## **Fields of Study**

Major Field: Materials Science and Engineering

Minor Field: Computer Science and Engineering- Artificial Intelligence and Machine Learning Track

## **Table of Contents**

		Page
Abstract		. ii
Dedicatio	n	. iii
Acknowle	edgments	. iv
Vita		. vii
List of Ta	bles	. xii
List of Fig	gures	. xvi
List of Al	obreviations	. xxvii
1. Intro	oduction	. 1
1.1 1.2 1.3 1.4	Deformation twinning in hcp metals	. 2 . 4 . 8 . 10
2. Ato arie	mistic modeling of dislocation interactions with symmetrical tilt grain bounds in titanium	- . 12
2.1 2.2 2.3	Introduction	. 13 . 15
2.3	aries	. 18 . 21
	boundary	. 21

		2.4.2	Interactions of the prismatic $\langle c \rangle$ edge and pyramidal mixed $\langle c + a \rangle$ dislocations with ( <b>1011</b> ) boundary	23
		2.4.3	Interactions of the prismatic $\langle a \rangle$ screw dislocation with ( <b>1013</b> ) boundary	27
		2.4.4	Interactions of the pyramidal $\langle \mathbf{c} + \mathbf{a} \rangle$ dislocation with ( <b>1013</b> ) boundary	- 29
		2.4.5	Interactions of the prismatic edge $\langle c \rangle$ dislocation with ( <b>1013</b> ) boundary	32
	2.5	Conclu	uding Remarks	34
3.	Slip-	induced	twinning from general (random) grain boundaries in titanium	38
	3.1	Introdu	uction	39
	3.2	Slip tra	ansfer and experimental analysis	40
	3.3	Comp	utational method	43
	3.4	Result	S	46
	3.5	Conclu	uding Remarks	53
4.	First in tit	-princip anium .	les prediction of oxygen diffusivity near the ( <b>1012</b> ) twin boundary	54
	4.1	Introdu	uction	55
	4.2	Comp	outational Method	57
	4.3	Site E	nergies	59
	4.4	Energy	y Barriers for Diffusion	63
	4.5	Diffus	ion coefficient	65
	4.6	Conclu	usion	71
5.	Quar	ntitative	analysis of uncertainty in self and solute diffusion calculations	- 4
	from	first-pri		/4
	5.1	Introdu	uction	74
	5.2	Uncert	tainty sources	76
	5.3	Comp	utational method	77
	5.4	Diffus	ion calculation	79
		5.4.1	Model	79
		5.4.2	Effects of exchange-correlation on diffusivities	81
		5.4.3	Effects of attempt frequencies on diffusivities	91
		5.4.4	Diffusivity in meta-stable phases	92
	5.5	Conclu	uding remarks	93

6.	Solu nami	te/Twin boundary interaction as a new atomic-scale mechanism for Dy- c Strain Aging: Interstitial diffusion
	6.1	Introduction
	6.2	Computational method
	6.3	Theory of solute effects on Twin Growth
		6.3.1 Role of solutes on disconnection glide
		6.3.2 Assessing the waiting time
		6.3.3 Model Predictions
7.	Solu	te/Twin boundary interaction as a new atomic-scale mechanism for Dy-
	nami	c Strain Aging: Vacancy-mediated diffusion
	7.1	Introduction
	7.2	Computational Methods
	7.3	Theoretical model of DSA
		7.3.1 Solute/twin boundary interaction model
		7.3.2 Solute/dislocation interaction model
	7.4	Effect of Al and Gd solutes on DSA in Mg
		7.4.1 Solute/vacancy binding near the twin boundary
		7.4.2 Solute/vacancy binding near the dislocation
		7.4.3 Model predictions
8.	Cond	clusion and Future Directions
	8.1	Summary of Results
	8.2	Limitations and Future Directions

## List of Tables

Tabl	le	P	age
2.1	Excess potential energy (PE) for three STGBs		17
2.2	Burgers vectors of ( $\overline{1}011$ ), ( $\overline{1}012$ ) and ( $\overline{1}013$ ) twinning dislocations in Ti- tanium (Å): Lattice parameter and $c/a$ ratio are: $a = 2.9304$ Å and $\kappa = 1.5964$ . $\rho_e$ , $b_{2e}$ , $b_{2s}$ , $b_{t,2}$ and $b_{t,4}$ are TD coefficient, 2-step edge, 2-step screw components, resultant 2-step height mixed and 4-step height pure edge Burgers vector, respectively. Sign convention in all following Burg- ers vector notations are right hand side start to finish convention.		20
4.1	Site energies for oxygen at different stable interstitial sites. The relative formation energy (eV) and the distance from the boundary $d(\text{\AA})$ for each site is listed (cf. Figure 4.1).	•	62
4.2	Attempt frequencies for different transition networks. The bulk values of the attempt frequencies correspond to the jumps in L4 layer, which represents the bulk-like environment compared with the same type of jumps in the vicinity of $(10\overline{1}2)$ TB (cf. Figure 4.1). The jump vector of each transition is indicated in the second column. $z$ is the Wyckoff coordinate of the tetrahedral sites along the $\vec{c}$ axis in a typical hcp lattice	•	65
4.3	Arrhenius fit to the diffusivity data derived from the diffusion model based on the solution to the master equation. Diffusivities are fit to the $D = D_0 \exp(-E_{act}/K_BT)$ equation over the temperature range of $600 - 1100$ K, where $D$ , $D_0$ and $E_{act}$ are diffusivity, diffusion prefactor and activation en- ergy barrier, respectively. These values are compared to our bulk-like re- gion calculation as well as previous analytical model [1]. These results show the decrease in the overall activation energy of jumps near the TB, therefore, higher rate of diffusion.		72

5.1	Migration barriers (eV) and attempt frequencies (THz) of jumps involved in the diffusion of Mg(Al) in fcc Al(Mg) within the five-frequency model [2]. Values calculated using ultra-soft pseudopotential (USPP) and the PBE functional are compared to the PAW with the PBEsol functional (PAW- PBEsol). Attempt frequencies from both density functional perturbation theory (DFPT) and finite difference method (FDM) using PAW-PBEsol functional are calculated and compared. Solute-vacancy nearest-neighbor binding energies are also listed.	82
5.2	Migration barriers (eV) and attempt frequencies (THz) for the diffusion of dilute Mg(Al) in hcp Al(Mg) from the 1b configuration following the notation in reference [3]. Migration barriers from previous DFT works are also included for comparison (cf. Figure 5.2 for notation and the caption in Table 5.1 for DFT settings interpretation).	83
5.3	Migration barriers (eV) and attempt frequencies (THz) for the diffusion of dilute Mg(Al) in hcp Al(Mg) from the 1p configuration following the notation in reference [3]. Migration barriers from previous DFT works are also included for comparison (cf. Figure 5.2 for notation and the caption in Table 5.1 for DFT settings interpretation).	84
5.4	Migration energies (eV) and attempt frequencies (THz) for vacancy medi- ated diffusion in elemental fcc/hcp Al and Mg. For hcp systems, the values for basal and (pyramidal) jumps are shown without and (with) parentheses. For DFT settings tags interpretation, refer to the caption in the text and Table 5.1.	85
5.5	Vacancy formation energies and vacancy formation entropies in fcc/hcp Al/Mg systems using different DFT settings. For Al cells, results from regular PAW-PBE functional are also reported	85
5.6	Arrhenius fit to the calculated self-diffusion coefficients. Diffusivities are fit to the $D = D_0 \exp(-E_{act}/k_BT)$ equation, where $D$ , $D_0$ , and $E_{act}$ are diffu- sivity, diffusion prefactor and activation energy barrier, respectively. These values are compared to the experimental values reported in the literature, For Al systems, fit to the diffusivity data derived from regular PAW-PBE functional for vacancy formation energies and entropies are also included. For hcp systems, diffusivity values for basal and ( $\vec{c}$ ) are shown without and (with) parentheses. For DFT settings tags interpretation, refer to the cap- tion in the text and Table 5.1.	89

5.7	Arrhenius fit to the calculated impurity diffusion coefficients. Diffusivities are fit to the $D = D_0 \exp(-E_{act}/k_BT)$ equation, where $D$ , $D_0$ , and $E_{act}$ are diffusivity, diffusion prefactor and activation energy barrier, respectively. These values are compared to the experimental values reported in the litera- ture. For Al systems, fit to the diffusivity data where the regular PAW-PBE functional is used to calculate vacancy formation energies and entropies are also included. For hcp systems, diffusivity values for basal and ( $\vec{c}$ ) are shown without and (with) parentheses. For DFT settings tags interpreta- tion, refer to the caption in the text and Table 5.1.	90
7.1	Al solute/twin boundary binding (driving force), vacancy formation energy added to the solute/vacancy binding, migration energy barriers, activation enthalpies and the attempt frequencies for the jumps into/within the twin boundary in Mg evaluated from DFT, respectively. Energy values are reported in eV and the attempt frequencies are in THz. Forward-fw (backward-bw) values correspond to the jumps in the direction (opposite direction) of the arrowheads in Figure 7.1. Basal and pyramidal jumps within the bulk values are also included for comparison. Negative values show the attractive binding.	128
7.2	Gd solute/twin boundary binding (driving force), vacancy formation en- ergy added to the solute/vacancy binding, migration energy barriers, ac- tivation enthalpies and the attempt frequencies for the jumps into/within the twin boundary in Mg evaluated from DFT, respectively. Energy values are reported in eV and the attempt frequencies are in THz. Forward-fw (backward-bw) values correspond to the jumps in the direction (opposite direction) of the arrowheads in Figure 7.1. Basal and pyramidal jumps within the bulk values are also included for comparison. Negative values show the attractive binding	129
7.3	Numerical values used for evaluating DSA from twin segregation model formulated in Equation 7.2 for Al and Gd solutes in Mg	130
7.4	Numerical values used for evaluating DSA from solute/dislocation interac- tion model formulated in Equation 7.4 for Al and Gd solutes in Mg	130

## List of Figures

Figu	re	Pa	ge
1.1	Basal, prismatic and pyramidal slip modes with (a) $\langle a \rangle$ -type and (b) $\langle c+a \rangle$ -type Burgers vector in hcp Ti. Pyr. I and Pyr. II denote to the pyramidal-I and pyramidal-II planes, respectively.		3
1.2	Critical resolved shear stress for $\langle a \rangle$ and $\langle c + a \rangle$ Burgers vectos slips as a function of temperature in single crystal Ti-6.6Al. The figure is adapted from [4].		3
1.3	Twinning planes and the corresponding shear directions of possible twin modes in Ti activated under the tension or compression along the $\vec{c}$ axis. Pyr. I and Pyr. II indicate the pyramidal-I and pyramidal-II planes, respectively.		5
1.4	The engineering stress-displacement curves of the compression tests at dif- ferent oxygen concentrations in Ti. The figure is adapted from [5]		6
1.5	True tensile stress versus true strain curves for Ti single crystals that are favored for $(10\overline{1}2)$ twinning tested between 78 and 773 K. The figure is adapted from [6].		8
2.1	Schematic representation of $(\bar{1}011)$ , $(\bar{1}012)$ and $(\bar{1}013)$ planes sharing common zone axis $[\bar{1}2\bar{1}0]$ in an hcp crystal structure.		14
2.2	Structure and potential energy (PE) per atom for three STGBs in Ti: (a)-(b) ( $\overline{1}011$ ) TB, (c)-(d) ( $\overline{1}012$ ), (e)-(f) ( $\overline{1}013$ ) TB. The color coding the left columns shows the potential energy of each atom. In the right column, common neighbor analysis is shown where the blue and red colors present hcp bulk and non-hcp structure indicative of the interface, respectively.		16

2.3	Bicrystal cell for dislocation/boundary simulations: two grains are indi- cated with red and blue atomic colors, respectively. Atoms in green color are fixed in their positions during relaxation.	17
2.4	Dichromatic pattern for (a) ( $\overline{1}011$ ) and (b) ( $\overline{1}013$ ) twin boundaries. $t_{\lambda}$ and $t_{\mu}$ are the translation vectors for generating the step character. Two and four step height dislocation Burgers vectors are shown in this figure. Blue and red color atoms are representative of $\lambda$ and $\mu$ crystallographic orientations which are mirrored about the boundary planes. Yellow colored atoms correspond to the $\lambda$ crystallographic orientation repeated through entire cell to construct dichromatic pattern. $\vec{b_2}$ and $\vec{b_4}$ denote two step and four step Burgers vectors, respectively.	19
2.5	$(\bar{1}011)$ , $(\bar{1}013)$ and $(\bar{1}012)$ Twinning dislocations in Ti: (a),(c) 2 and 4-step height ( $\bar{1}011$ ) TB. (b),(d) 2 and 4-step height ( $\bar{1}013$ ) TB. (e) 2-step height ( $\bar{1}012$ ) TB. Color coding is the common neighbor analysis (CNA) [7]. Blue atoms have hcp coordinates while red atoms show the defective regions	20
2.6	Interactions with ( $\overline{1}011$ ) TB. (a) Glissile twinning dislocations are created on the boundary as a result of an $\langle a \rangle$ screw dislocation. (b) $\gamma_{xy} = -0.011$ shear strain is applied which moves the twinning dislocation. (c) presents the interaction of an $\langle c \rangle$ prism edge dislocation with the boundary under no shear strain. (d) Applying $\gamma_{xy} = -0.01$ , $\gamma_{yz} = -0.0083$ shear strains cre- ates two twinning dislocations as well a dissociated lattice dislocation the adjacent grain. (e) depicts the $\langle c + a \rangle$ mixed pyramidal dislocation interac- tion with the ( $\overline{1}011$ ) boundary with no shear strain. (f) shows that applying $\gamma_{yz} = -0.01$ shear strain results in nucleation of a twinning dislocation and an extended lattice dislocation in the adjacent grain, similar to (d). $b_{t,2}$ , $b_{st}$ and $b_r$ are 2-step height ( $\overline{1}011$ ) TD, Shockley partial and the residual dislocation respectively.	22
2.7	Nye tensor analysis on the partial dislocations corresponding to the stack- ing fault in the second grain: (a) $\langle c \rangle$ prism edge (b) $\langle c+a \rangle$ pyramidal mixed dislocation interactions with ( $\overline{1}011$ ) STGB. Edge components (c)-(d) and Screw components (e)-(f) of the partial dislocation which is passed through the boundary is plotted for $\langle c \rangle$ and $\langle c+a \rangle$ dislocations, respectively. This shows that for both cases, the leading partials is pure edge, suggesting the nucleated $\langle a \rangle$ dislocation must be of mixed type.	26

xvii

2.8	Possible dissociation scenarios for an $\langle a \rangle$ dislocation on basal planes. In all	
	of our dislocation/boundary interaction simulations, line direction is fixed	
	and is chosen along $[\bar{1}2\bar{1}0]$ . Burgers vector AB corresponds to a screw	
	dislocation, while Burgers vectors AC or BC correspond to mixed type	
	dislocations. Further analysis of possible Shockley partial Burgers vectors	
	reveal that only $\delta C$ is of pure edge character. This partial dislocation can	
	only be created by dissociation of a mixed $\langle a \rangle$ dislocation, i.e AC or BC 27	7

2.13	Prismatic edge $\langle c \rangle$ dislocation interaction with the ( $\bar{1}013$ ) boundary. (a) Relaxed geometry is shown under no applied strain. A well-defined ( $\bar{1}012$ ) twin embryo is nucleated in the neighboring grain (b) Additional defects are created upon application of $\gamma_{yz} = -0.03$ shear strain. The insets in (c)- (f) provide a closer look at these defects as follows. (c) 2-step height ( $\bar{1}013$ ) TD, (d)-(e) ( $\bar{1}012$ ) twin embryo and a dissociated basal dislocation in the second grain and (f) 2-step, 4-step height and zigzag kinks on the bound- ary. Basal-Prism facet as well as ( $\bar{1}012$ ) TD is represented on the twin embryo. $b_{edge}$ , $b_{t,2}$ , $b_{t,4}$ , $b_{t,\bar{1}012}$ and BP show $\langle c \rangle$ edge, 2-step, 4-step height ( $\bar{1}013$ ) twinning, ( $\bar{1}012$ ) twinning dislocations and Basal-Prism interface, respectively.	35
2.14	Nye tensor analysis on the basal dislocation, nucleated from the interaction of a prismatic $\langle c \rangle$ edge dislocation with the ( $\overline{1}013$ ) boundary. (a) Shows a section of Figure 2.13. The dissociated dislocation is magnified in (b) and reoriented such that basal planes are aligned horizontally. Edge and screw components are shown in (c) and (d), respectively. The partial dislocations have the same edge component, with opposite signs, and the same sign screw component. The Nye tensor analysis shows that both partials are mixed type dislocations, suggesting that the original $\langle a \rangle$ type dislocation must have been of screw character.	36
3.1	Correlation of a large number of slip transmission (S), twinning (T) and no event (0) as a function of Schmid factor for twinning $(m_t)$ and Morris and Luster slip transmission parameter $(m')$ . Outlier cases are indicated with red circles. (Adapted from [8])	42
3.2	SEM-level analysis by Mills group at OSU [9] of an outlier case where slip in grain 1 initiated pyramidal slip in grain 2 with no twin activity observed.	43
3.3	Bicrystal setup in MD simulations sliced along <i>Y</i> . The grain orientations and grain boundary plane indicated in this figure are chosen based on the experimental measurements. Blue and red color shows the inner cube with free atoms and outer layer with 20 Å thickness of fixed atoms in all directions, respectively.	44
3.4	Grain boundary structure optimization. (a) Shows the excess grain bound- ary energy of bicrystal with different cell dimensions. (b) Shows the mi- croscopic degrees of freedom associated with the grain boundary structure known as <i>t</i> -space	45

3.5	The effect of microscopic degrees of freedom on GB excess energy. (a) and (b) Show the 3D and the cross section of energy map constructed by sliding top grain with respect to the lower grain, respectively.	46
3.6	Interaction of imposed prismatic loop in the lower grain and the random grain boundary. Snapshots of simulations depicted after (a) 0, (b) 400, (c) 1600 and (d) 2400 relaxation steps under the applied strain with the resolved shear strain component of $\gamma_{RSS} = 0.0355$ on the prismatic loop plane. Non-hcp atoms are only shown to avoid confusion. Green ribbon shows the thickness of 20 Å where atoms are fixed in positions.	47
3.7	Analysis of the generated defect in grain 2 as a result of $\langle a \rangle$ -type prismatic loop and GB interaction. (a) shows the generated defect reoriented such that X and Z are along $\frac{1}{3}[2\overline{1}\overline{1}3]$ and $(\overline{2}112)$ directions, respectively. (b) shows the slip of atoms on the {1011} pyramidal-I plane within the parent hcp lattice orientation where { $\overline{2}112$ } pyramidal-II planes lie on XY plane presented in (c).	48
3.8	Local crystallographic orientation analysis of the generated defect in grain 1 using common neighbor analysis. (a) depicts the generated defect within hcp atoms colored in purple and the hcp atoms colored in red which are removed in (c) to only show the defect. (b) and (c) enlarges the enclosed region which shows multiple partial dislocations cross-slip, leaving behind basal stacking fault regions colored in green. Misorientation analysis shows that hcp atoms are reoriented within the grain and the defect colored in purple acts as a basal-to-prismatic interface.	50
3.9	Analyzing the dislocation characters within the bicrystal. Generated dislo- cations in the grain 2 are mainly characterized as $\frac{1}{9}\langle 2\bar{2}0\bar{3}\rangle$ , $\frac{1}{3}\langle 1\bar{1}00\rangle$ basal Shockley partial and $\frac{1}{9}\langle 1\bar{1}03\rangle$ . Other type of partial dislocations are iden- tified which embrace less than 9% of total dislocations length and catego- rized as <i>other</i> .	51
3.10	Dislocation analysis of the generated defect around the stacking fault. (a,d) and (b,c) represent the dislocation Burgers vector character and type (screw,edg respectively. Nucleated dislocations dissociate into partials leaving behind stacking faults (colored in green) on the basal planes.	e), 52

- Twin geometry supercell. (a)  $X([\bar{1}011])$  and  $Y([1\bar{2}10])$  directions are twice 4.1 and three times the single periodicity of the twin geometry unit cell, respectively. This supercell is used for all of the site energy and transition barrier calculations. The stable octahedral, crowdion, hexahedral and tetrahedral sites for oxygen are indicated by O (red), C (green), H (light brown) and T(grey), respectively. Dotted red line encloses the cell used for the diffusion coefficient calculation in the Section 4.5. (b) The inset shows a magnified view of the positions of all the nonequivalent stable sites within the supercell. All other sites can be obtained from these positions by symmetry and are considered in constructing the transition network and diffusion calculations. The crowdion sites, indicated in the parentheses, are located at different depths along the Y direction compared to the nearby octahedral sites. L1-L4 label the atomic layers from the closest layer to the TB to the bulk-like region away from the boundary. The star shows the bulk-like reference octahedral site used for the site energy calculations. Oxygen at H2 hexahedral site relaxes to the nearby tetrahedral. The black triangle shows the unstable crowdion site near the twin boundary. The distortion of host atoms due to the relaxations is not shown here to avoid confusion. 59
- 4.5 Potential energy surface (PES) of oxygen along {1012} twin boundary. Incorporating the symmetry of the cell, PES calculations are performed on the smallest periodic unit of the twin boundary plane, depicted in the left figure. Relative formation energies for oxygen are given in eV. . . . . . . . 63

4.4	Transition energy barriers for ( <i>a</i> ) octahedral to octahedral and octahedral to tetrahedral, ( <i>b</i> ) octahedral to hexahedral, ( <i>c</i> ) octahedral to crowdion and tetrahedral to crowdion, and ( <i>d</i> ) hexahedral to crowdion jumps. The energy barriers are calculated between interstitial sites at various distances from the twin boundary from L1, closest layer to the boundary to L4 where bulk structure is retrieved. Dashed lines in each figure show the corresponding transition barrier in bulk. Note that tetrahedral sites are only stable in L1 and L2. Due to the shallow barrier of jumps from crowdion sites in L1 and L2 layers, C1-C4 are excluded as metastable sites from network. The L1 barriers indicated in ( <i>c</i> ) – ( <i>d</i> ) correspond to the jumps with crowdion sites located on the twin boundary as one of the metastable sites	66
4.5	Isotropic diffusion in bulk hcp $\alpha$ -Ti. We compare the diffusivity evaluated using the master equation based diffusion model implemented in the current study with the previously reported multi-state diffusion model in hcp bulk $\alpha$ -Ti [1]. Very close values of the diffusivity in both basal plane and along the $\vec{c}$ axis of hcp cell suggests the nearly isotropic diffusion in bulk hcp $\alpha$ - Ti. <i>Y</i> axis in the figure is in logarithmic scale. The experimental data from the literature is also depicted for the sake comparison[10, 11]	68
4.6	Diffusivity in bulk hcp $\alpha$ -Ti compared to a previous DFT calculation [1] and experimental predictions[10, 11]. Our diffusivity values are in good agreement with the reported Multi-state-Diffusion-based diffusivity by Wu and Trinkle [1].	69
4.7	Diffusion coefficient in the presence of TB. Diffusivity along three lattice directions in the twin geometry is compared with the bulk diffusivity in a logarithmic scale. It is shown that the diffusivity increases near the TB. The green and black dashed lines show the Arrhenius fit to the diffusion coefficient data along the direction in and perpendicular to the TB, respectively.	71
4.8	Contribution of tetrahedral interstitial sites in the oxygen diffusion near the TB. (a) filled symbols show the diffusion coefficients evaluated by considering the tetrahedral sites in the network (the same data as depicted in Figure 4.7) compared to the diffusivity without considering the tetrahedral sites in the network. Bulk diffusion is also included for comparison. (b) the ratio of computed diffusivity using the network with tetrahedral sites to the network without tetrahedral sites. This shows including the tetrahedral sites in the diffusion network has a more highlighted impact on the diffusivity toward the TB compared to other two directions.	72

5.1	Five-frequency jumps in fcc crystal structure. Solute and vacancies are indicated by yellow sphere and white square, respectively. Blue spheres represent host atom.	81
5.2	Atomic hops considered in the diffusion model in hcp (based on the nota- tions in [3]). Top and bottom rows show the basal and pyramidal jumps, respectively. Schematics in the left and right columns represent the solute and vacancy on the same plane (1b) and solute and vacancy on the different plane (1p), respectively. Note that the two reorientation jumps from 1b, that have been treated as a unique jump in previous models, are distinguished by 1b-1b in blue and <u>1b-1b</u> in yellow in the top left figure. Solute and va- cancies are indicated by yellow sphere and white square, respectively. Blue spheres represent host atom (modified after [3]).	86
5.3	Self diffusion coefficients for fcc Al and hcp Mg. DFT results derived from different exchange-correlation pseudopotentials and attempt frequency calculation methods are compared with the experimental assessment in reference [12]. For Al systems, diffusivity results with the vacancy formation energy and entropy evaluated from regular PAW-PBE is also shown	87
5.4	Impurity diffusion coefficients: (a) Mg in fcc Al and (b) Al in hcp Mg. DFT results derived from different exchange-correlation pseudopotentials and attempt frequency calculation methods are compared with the experimental assessment in reference [12]. For Al systems, diffusivity results with the vacancy formation energy and entropy evaluated from regular PAW-PBE is also shown.	88
5.5	Diffusion coefficients in metastable phases: (a) self-diffusivities in elemen- tal hcp Al and fcc Mg, (b) impurity diffusion of Al in fcc Mg and Mg in hcp Al using the optimized DFT settings identified for stable phases as explained in the text.	92

6.1	Twin growth by formation of a square twinning dislocation loop: (a)-(b) show the lateral growth of twin by island formation. (a) is the cross-section of twin loop and (b) is the view normal to the twin boundary. (c)-(e) show the twin growth where the solutes can segregate to and pin the boundary (c). Upon applying a large enough stress, the twin boundary can escape the solute environment and grow by forming a new loop (d). If the solutes can diffuse fast enough to reach the new twin boundary, this process can repeat (e). Red atoms indicate the interstitial solutes and the dashed lines are twin boundaries.	. 101
6.2	Twin boundary geometry and minimum energy paths for oxygen segrega- tion. Oxygen atoms at the octahedral, crowdion, tetrahedral and hexahedral sites are shown by the symbols O, C, T and H, respectively. The arrows show the minimum energy path for oxygen atom jumps from octahedral sites in L1 layer to the lowest energy octahedral sites at the TB, L0 result- ing in the segregation. Labels for the sites located behind octahedral sites are indicated in the parenthesis	. 103
6.3	(a) Position of <i>all</i> stable oxygen interstitial sites around $(10\overline{1}2)$ twin bound- ary. Octahedral, crowdion, tetrahedral and hexahedral sites are shown by the symbols O, C, T and H, respectively. (b)-(e) relative energy barriers corresponding to the different possible paths between octahedral sites from L1 to L0. Transport occurs via meta-stable interstitial sites. Each of the meta-stable sites is indicated with a scatter symbol and the peak between each two symbol corresponds to the transition state energy derived from the nudged elastic band calculations.	. 104
6.4	Twin growth modes: (a) lateral growth of twin from state (1), fully segre- gated coherent twin boundary (green dashed line), to state (2), twin loop nucleation (green solid line) and (b) Longitudinal growth of twin discon- nection from the fully segregated state: (a) migration of disconnection from state (1), fully segregated solutes to the boundary (green dashed line), to state (2), disconnection glide represented for a single periodic unit (green solid line). Color coding shows the common neighbor analysis (CNA) [13]. White atoms have hcp coordinate while black atoms show the defective re-	
	gion. Solutes are colored as red atoms.	. 107

6.5	Solute interaction with twinning disconnection: (a) shows the DFT simulation cell set up comprising of coherent twin boundary connected by twin disinclination and (b) shows the twinning disconnection with a step and dislocation character and possible octahedral interstitial sites for oxygen near the disconnection. Color coding shows the common neighbor analysis (CNA) [13]. White atoms have hcp coordinate while black atoms show the defective region.	. 109
6.6	Variation of strength with strain rate at various temperatures and initial oxygen content in Ti. (a) shows prediction of present model at $T=423$ K for various oxygen contents and (b) shows the strength predictions at various temperatures. Dashed vertical lines show the experimental strain rate reported in [6].	. 112
7.1	$(10\overline{1}2)$ twin boundary geometry in Mg, possible substitutional sites and the paths between solute/vacancy jumps for (a) Al and (b) Gd. Green arrows show the jumps in the direction of attractive solute/twin boundary binding driving force and red arrows show the repulsive binding energy. Solutes tend to move in the direction of attractive thermodynamic binding. Attractive sites for the solutes are underlined in the figure.	. 123
7.2	Solute/dislocation interaction energies and the difference between the in- teraction energies at the compression and the tension sides of basal edge dislocation core for (a,c) Al and (b,d) Gd in Mg calculated using the ana- lytical model explained in [14]. Al (smaller than Mg) and Gd (larger than Mg) solutes tend to reside in the compression and tension sides of disloca- tion core, respectively.	. 131
7.3	Nye tensor analysis on the basal edge dislocation core of Mg using Liu [15] empirical potential at 0 K. (a) shows the edge component and (b) shows the screw component of the dissociated partials, respectively.	. 133
7.4	Cross-core diffusion of Al in Mg basal edge dislocation evaluated using empirical potential molecular statics. Possible substitutional sites around the dislocation core and the paths between them are illustrated. Paths (1) and (2) denote cross-core jumps and the (3) and (4) denote within the compression and tension sides of core, respectively.	. 134

Additional strengthening due to the solute/twin boundary interaction (solid
lines) compared to the solute/dislocation interaction (dotted lines) for (a)
Mg-0.90at% Al and (b) Mg-0.24at% Gd. Change in the additional strength-
ening at the given strain-rate and temperature demonstrates the dynamic
strain aging mechanism

## List of Abbreviations

BP	Basal-to-Prism
CRSS	Critical Resolved Shear Stress
DFT	Density Functional Theory
DOF	Degree of Freedom
DSA	Dynamic Strain Aging
EAM	Embedded Atom Model
FCC	Face Centered Cubic
GB	Grain Boundary
GGA	Generalized Gradient Approximation
НСР	Hexagonal Close-Packed
КМС	Kinetic Monte Carlo
LDA	Local Density Approximation
MD	Molecular Dynamics
MEAM	Modified Embedded Atom Model

- MEP Minimum Energy Path
- MS Molecular Statics
- MSD Multi-State Diffusion
- NEB Nudged Elastic Band
- nSRS Negative Strain Rate Sensitivity
- PAW Projector Augmented Wave
- PBE Perdew-Burke-Ernzerhof GGA Exchange-Correlation
- PLC Portvein-LeChatelier
- QHA Quasi Harmonic Approximation
- RSS Resolved Shear Stress
- SEM Scanning Electron Microscope
- STGB Symmetrical Tilt Grain Boundary
- TB Twin Boundary
- TD Twinning Dislocation
- TEM Transmission Electron Microscope
- USPP Ultrasoft Pseudopotential
- XC Exchange-Correlation

### **Chapter 1: Introduction**

One of the major goals of the science and engineering community is increasing both strength and ductility of structural materials. Traditional methods for strengthening rely on the controlled generation of internal defects, and thereby increase in strength at the cost of reducing ductility and toughness. Defects are typically categorized into: point defects - vacancies or interstitials- where an atom is missing from a perfect crystal or an atom occupies a site within the perfect crystal, line defects -dislocations- around which a line of atoms are missing or misaligned, and planar defects -grain boundaries, stacking faults or twin boundaries- that can be treated as 2D interfaces. Presence of defects in crystalline materials is inevitable, yet these defects can be controlled to improve the mechanical properties. Accurate study of these defects via computational methods provide invaluable tools to identify their role on mechanical and electronic properties of materials.

Titanium (Ti) and its alloys have high demand in biomedical, automotive, and aerospace industries due to their relatively light weight, high strength and corrosion resistance. The low temperature phase of Ti, known as  $\alpha$ -Ti, has a hexagonal close-packed (hcp) crystal structure with lattice parameters of a = 2.93 Å, c = 4.61 Å and a c/a ratio of 1.577, which is lower than the ideal value of 1.633 for a close-packed lattice. Unlike cubic crystal structures, the deformation of hcp materials is anisotropic meaning that the mechanical properties in this class of materials depend on the direction of loading. In strengthening processes, the trade-off between increasing ductility and strength is attributed to the anisotropic plastic deformation in hcp materials. Low-temperature ductility of this class of materials is linked to twinning- an important deformation mechanism where the number of active slip systems is limited. In ductile Ti, more than one twin system is active under both tension and compression while in less ductile metals, such as magnesium (Mg), only one twinning mode is operative. The aim of this dissertation is to understand the fundamental reasons underlying different twinning behaviors by comparing the twin nucleation and growth mechanisms in pure and alloyed hcp metals.

#### **1.1 Deformation twinning in hcp metals**

The mechanical properties of hcp metals are strongly dependent on the combination of active deformation modes, both slip and twinning. Slip system is defined as the set of symmetrically identical slip planes and associated family of slip directions for which dislocation motion can easily occur and lead to plastic deformation. The two most likely Burgers vectors in hcp crystals are  $\langle a \rangle$  and  $\langle c + a \rangle$ . Possible slip systems for both slip directions are shown in Figure 1.1. Figure 1.2 compares the critical resolved shear stress (CRSS) for activation of  $\langle a \rangle$ -type slip on basal and prism planes with  $\langle c+a \rangle$ -type pyramidal slip in a Ti alloy. CRSS is the resolved component of applied stress which starts moving the dislocation and is a measure of slip system activity. As shown in Figure 1.2,  $\langle a \rangle$ -type slip on prism planes requires the lowest CRSS over the range of temperatures and therefore is the easiest deformation mode to activate in Ti.

In 1928, it was von Mises who first pointed out that for a polycrystalline material to be able to undergo ductile plastic deformation, five independent slip systems are necessary [16]. To satisfy the von Mises criterion under the constraint that  $\langle a \rangle$ -type slip is restricted,



**Figure 1.1:** Basal, prismatic and pyramidal slip modes with (a)  $\langle a \rangle$ -type and (b)  $\langle c + a \rangle$ -type Burgers vector in hcp Ti. Pyr. I and Pyr. II denote to the pyramidal-I and pyramidal-II planes, respectively.



**Figure 1.2:** Critical resolved shear stress for  $\langle a \rangle$  and  $\langle c + a \rangle$  Burgers vectos slips as a function of temperature in single crystal Ti-6.6Al. The figure is adapted from [4].

ductile deformation is accommodated by activation of the  $\langle c+a \rangle$  slip mode and deformation twinning. Deformation twinning is a process in which a part of the crystal undergoes a homogenous shear such that it produces the original crystal structure in a new orientation. The interface between these two crystals -twin boundary- is a highly symmetrical interface, often with one crystal called "twin" oriented as the mirror image of the parent crystal called "matrix". The surface along which the lattice points are shared between the matrix and twin crystals is called twinning plane.

Various twin activities have been observed under applied tension or compression parallel to the  $\vec{c}$  axis. Figure 1.3 shows the possible twinning planes and shear directions for different twin modes in Ti. The {1012} and {1121} modes are activated during tension while the {1011} and {1122} modes are activated during compression. Among those, {1012} is the most commonly observed twin in Ti.

## **1.2** Improving mechanical properties via alloying

One of the most effective methods to improve or control the mechanical properties of materials is by alloying and chemistry change. Despite brilliant mechanical features, Ti sees limited use at high temperatures due to its high reactivity with oxygen (O) requiring expensive steps to prevent oxidation. On the other hand, this high oxygen reactivity leads to the rapid formation of stable oxide layers, providing high corrosion resistance [1]. Increasing the oxygen content also enhances the tensile strength of Ti, but has a detrimental effect on the ductility [17]. The strengthening mechanisms in Ti are mostly based on the role of solutes on hindering the dislocation motion. This is also true for oxygen atoms which hinder the dislocation motion and low temperature twinning. Figure 1.4 depicts



Figure 1.3: Twinning planes and the corresponding shear directions of possible twin modes in Ti activated under the tension or compression along the  $\vec{c}$  axis. Pyr. I and Pyr. II indicate the pyramidal-I and pyramidal-II planes, respectively.

the engineering stress-displacement curves for Ti samples with different oxygen concentrations from different nano-compression tests captured from *in situ* transmission electron microscopes (TEM) analyses [5]. As shown, the Ti-0.1wt% O sample exhibited the lowest strength, but with substantial work hardening upon yielding. By enhancing the O content to 0.3wt%, the yield strength increased to 2.5 GPa, which is 8 times greater than for Ti-0.1wt% O ( $\sim$  320 MPa). However, this incredible increase in strength of Ti comes at the cost of reducing ductility, which is associated with the suppression of twinning in the presence of oxygen in Ti alloys. The mechanism underlying the twin suppression in the presence of oxygen solutes has remained an open question in the literature. Therefore, understanding the effect of oxygen and other alloying elements on the twin nucleation and growth is an important research area.



**Figure 1.4:** The engineering stress-displacement curves of the compression tests at different oxygen concentrations in Ti. The figure is adapted from [5].

It is generally believed that twins grow rapidly; however, previous studies show the very slow growth of twins in the presence of impurities [18, 19, 20, 21]. It has been reported that the increase in oxygen solutes leads to further suppression of  $\{10\overline{1}2\}$  twinning at low temperatures [22]. The study performed by Oberson *et al.* suggests that twinning in  $\alpha$ -Ti is controlled by the diffusion of oxygen *away* from the boundary [19]. They attributed the slow growth of the twins to the time necessary for repositioning of the octahedral sites occupied by oxygen atoms due to the shear and shuffle mechanism during the twin formation. However, this crystallographic study does not take into the account any of the energetic analysis in the interaction between oxygen atoms and the neighboring Ti atoms. Consequently, identifying the responsible mechanisms for twin suppression in presence of

oxygen solutes requires quantitative and accurate description of energetics as well as solute diffusivities near the twin boundaries.

Another important effect of solutes on mechanical properties of metals is the serrated flow phenomenon. Many dilute solid solutions exhibit the Portvein-LeChatelier effect (PLC) in technologically important metals. This phenomenon occurs at certain strain-rate and temperature conditions in which inhomogeneous deformation is observed, dominated by strain localization which leads to the serrated stress-strain curves. PLC is the macroscopic pattern associated with dynamic strain aging (DSA), which causes stress flow instability in the presence of solutes. DSA has been previously attributed to dislocations pinned by the solutes by forming a Cottrell atmosphere. Some experimental evidence interestingly identified the occurrence of DSA in single crystals oriented in favor of twinning in Ti-O [6] and Mg-rare earth elements alloys [23, 24, 25]. Figure 1.5 is selected from [6] and shows the appearance of serrated flow at higher temperatures in single crystal Ti samples with active {1012} twin deformation mode. DSA in Ti has also been characterized in other experimental studies, and is believed to be caused by diffusion of interstitial elements such as O and carbon (C) [26, 27]. This suggests that similar to the solute/dislocation interaction, solutes can segregate to the twins, pin them and thereby impede the twin growth resulting in DSA. To study this phenomenon, it is important to investigate the role of solute pinning on the twin growth.

The overarching goal of this dissertation is (1) to provide a systematic framework to study the mechanisms underlying the twin nucleation and growth in Ti; (2) to obtain a complete and quantitative picture of thermodynamics and kinetics of oxygen near Ti twin boundaries and the effect of oxygen on the mobility of twinning dislocations; and (3) to


**Figure 1.5:** True tensile stress versus true strain curves for Ti single crystals that are favored for  $(10\overline{1}2)$  twinning tested between 78 and 773 K. The figure is adapted from [6].

understand the strengthening effects due to solute segregation to the twin boundaries and the corresponding impact on dynamic strain aging.

### **1.3 Modeling techniques**

Over the past two decades, the growing power of computers has supplied a great incentive to the development of methods and code interfaces to tackle a vast range of scientific issues and provided robust computational tools. At the atomistic level, the two most common approaches to model the interaction between atoms are classical simulations using empirical interatomic potentials and *ab-initio* quantum mechanical methods. Molecular dynamics (MD) and molecular statics (MS) are the two common methods to follow the motion of atoms or determine their equilibrium position. With empirical potentials, classical MD and MS can treat very large numbers of atoms, whereas when using *ab initio* forces, the system size is much more limited. These methods are based on linking the forces to acceleration using Newton's equation of motion [28, 29]. The relaxed (ground state) configuration of atoms is found by minimizing the total energy of a system using conjugate gradient or other numerical approaches. In classical MD and MS, interatomic potentials are used, which are obtained by fitting to the experimental or quantum mechanical databases with crystal structure and physical property data. Since interatomic potentials have traditionally been fitted to properties of perfect crystals or at best simple defects such as point defects, they often have only limited transferability to systems with defects such as dislocations, impurities or stacking faults. Making interatomic potentials that reproduce extended-defect properties well is an active research area and frequently uses DFT-results for defect structures as fitting data.

Modern first-principles *ab initio* methods are typically based on Kohn-Sham density functional theory (DFT)[30]. In DFT, the energy and interatomic forces are calculated from the energy-minimized electron distribution around a given set of ion cores using quantum mechanics. Thus, no potentials need to be fitted, and changing interactions around defects, interfaces, solutes, etc., can naturally be described "out of the box" for more or less all elements of the periodic table up to the actinides, which is not possible in classical methods. In order to make this approach feasible for system sizes beyond a few atoms, which is needed for solid-state simulations, electrons are described by their density distribution and not by their wave functions, which is exact for the ground state (Hohenberg-Kohn theorem [31]). The most common iterative approach to find the ground state density is based on the Kohn-Sham equations [30]. Since this approach is fundamentally a single-particle-in-an-effective-field approach, it eliminates all many-body interactions such as exchange (which is expressed mostly in spin-interactions- no magnetism would be possible without exchange) and electronic correlations, without which especially the behavior of the electrons in *d* and *f*- orbitals often can not be described satisfactorily. To include these effects

into DFT calculations, a number of exchange-correlation functionals have been proposed in the literature. The most commonly used functionals are based on the local density approximation (LDA) and the generalized gradient approximation (GGA) [32, 33]. In our work, the electronic structure modeling is mostly done with the Vienna ab initio simulation package (VASP) [34], which is a modern plane wave basis density functional code. VASP is a powerful tool to compute an approximate solution to the many-body Schrodinger equation. Due to the high computational cost of these calculations, simulation size is limited and cannot be incredibly large.

DFT methods can be used for all types of atomistic calculations, MD, structural relaxation, determination of kinetic parameters such as diffusion coefficients, binding energies, or vibrational properties and resulting free energies. More details about these methods will be provided in the following chapters where such methods will be applied.

#### 1.4 Scope

In the following chapters, a systematic framework is developed to study the twin nucleation and growth mechanisms in Ti and other hcp alloys. Chapter 2 explains twin nucleation mechanisms as a result of dislocation and symmetrical tilt grain boundaries interaction. Chapter 3 studies the twin nucleation mechanism from a random grain boundary due to the slip activity in an adjacent grain known as "slip-induced twinning". Chapter 4 presents DFT prediction of oxygen diffusion near the  $(10\bar{1}2)$  twin boundary in Ti. Here, a framework is developed to predict the diffusion rate of solutes around the twin boundaries from DFT evaluated site and transition energies and an exact solution to the master equation. Chapter 5 focuses on the uncertainty analysis involved in predicting diffusivities from first principles with an application to Mg/Al alloys in stable and metastable hcp and face-centered cubic (fcc) phases. Chapter 6 introduces the role of interstitial solutes segregation to the twin boundaries on the strain-rate and temperature dependence of twin growth. Chapter 7 extends the theory proposed for interstitial solutes to the vacancy-mediated substitutional solutes segregation to the twin boundary and the corresponding effects on the twin growth. The developed models predict the strain-rate and temperature conditions of dynamic strain aging in Ti and Mg alloys due to the solute/twin boundary interactions. Chapter 8 summarizes the results and discusses the future directions in this area of research.

# Chapter 2: Atomistic modeling of dislocation interactions with symmetrical tilt grain boundaries in titanium

The work described in this chapter is a modified version of the following reference that has been published by M.S. Hooshmand *et al.* M.H. performed all the simulations. M.G. and M.M. designed and supervised the project. Manuscript was written by M.H. and revised by M.G. and M.M.

**M.S. Hooshmand**, M.J. Mills, M. Ghazisaeidi, "Atomistic modeling of dislocation interactions with twin boundaries in Ti", *Modelling and Simulation in Materials Science and Engineering (2017)* (link)

Dislocation/grain boundary interactions play an important role in plastic deformation and mechanical properties of materials. Many fundamental material properties such as strength, ductility, fracture and damage evolution are affected by grain boundary structure. In this chapter, we study the interaction between prismatic screw  $\langle a \rangle$ , prismatic edge  $\langle c \rangle$ and pyramidal mixed  $\langle c+a \rangle$  dislocations with ( $\overline{1}011$ ) and ( $\overline{1}013$ ) twin boundaries in titanium using atomistic simulations. Depending on the slip systems, atomic structure of twin boundary and stress/strain states, different components are nucleated. In all of the cases, twinning dislocations transmit through the boundary. The results also show that in some cases, partial dislocations transmit through the boundary leaving behind a stacking fault in the second grain. In the case of  $\langle c \rangle$  and  $\langle c+a \rangle/(\overline{1}013)$  interactions, ( $\overline{1}012$ ) twin embryo is nucleated in the neighboring grain. This study outlines some of the mechanisms underlying twin formation in Ti.

#### 2.1 Introduction

Mechanical properties of materials, such as strength and ductility, are governed by dislocation motion. Grain boundaries (GB) may impede the dislocation motion, therefore increasing the strength of material. Allowing the mobility of dislocations enhances the ductility and also eases the plastic deformation accommodation. In addition, GBs can act as nucleation sites for other lattice defects. Depending on the interacting components, transmission, annihilation, absorption or immobilization of lattice dislocations at the boundary can occur. In this chapter, we present a systematic study of dislocation/boundary interactions in Ti.

Symmetrical tilt grain boundaries (STGB) are special type of grain boundaries with a mirror symmetry between two crystals rotated with respect to a particular axis on the boundary plane. Only the tilt axis and tilt angle are required to describe the crystallography of STGBs. Depending on the angle of rotations, STGBs are categorized to either low or high angle tilt grain boundaries. Among different active twin modes in hcp systems, three of them namely { $\bar{1}011$ }, { $\bar{1}012$ } and { $\bar{1}013$ } have been drawn so much attention and their activity have been reported in many experimental observations [35, 36, 37, 38, 39, 40]. Figure 2.1 shows the crystallographic planes corresponding to these twin modes sharing the same [ $\bar{1}2\bar{1}0$ ] tilt axis. { $\bar{1}011$ } and { $\bar{1}013$ } twins occur under uniaxial contraction for all c/a ratios along the *c*-axis, unlike { $\bar{1}012$ } twins.

Several groups have investigated the atomic structures of STGBs and dislocation/ boundary interactions in hcp systems both experimentally and computationally. Wang *et al.* studied the atomic structures of STGBs in Mg and Ti over the range of  $0^{\circ}$  to  $90^{\circ}$  tilt angles [41, 42]. In another study from the same group, interaction between  $\langle a \rangle$ -type basal dislocation pile-ups and GBs in Mg has been modeled using molecular dynamics [43]. Various



**Figure 2.1:** Schematic representation of  $(\bar{1}011)$ ,  $(\bar{1}012)$  and  $(\bar{1}013)$  planes sharing common zone axis  $[\bar{1}2\bar{1}0]$  in an hcp crystal structure.

studies on dislocation/GB interactions in other hcp systems have been done by Serra *et al.* [44, 45, 46]. There is also substantial evidence from transmission electron microscopy [47, 48] and theoretical analysis [39, 49, 50] that facet nucleation and disconnections play important roles on the plastic deformation mechanisms. A review paper by Kacher *et al.* experimentally observed that the glissile components nucleated from the dissociation of incoming dislocation on the boundary can result in migration of twin boundary (TB), thereby thickening or thinning the twin region [51].

Despite various theoretical and experimental studies, twin nucleation mechanisms as a result of lattice dislocations other than  $\langle a \rangle$ -type basal have not been addressed in Ti. As

it is explained in Chapter 1, the dominant slip mode in Ti is prismatic  $\langle a \rangle$ -type slip. In addition, the relationship between twinning and  $\langle c \rangle$  or  $\langle c+a \rangle$  is essential in understanding the mechanistic theory underlying the slip stimulated twinning in polycrystalline materials. Through a systematic approach, we study the interaction of screw  $\langle a \rangle$ , prismatic edge  $\langle c \rangle$ and pyramidal mixed  $\langle c+a \rangle$  dislocations with ( $\overline{1}011$ ) and ( $\overline{1}013$ ) twin boundaries.

#### 2.2 Computational method

Dislocation/TB interactions in this study have been done using molecular dynamics approach at 0 K temperature. LAMMPS package [52] and a modified embedded atom method (MEAM) potential for Ti [53] have been implemented. This potential reproduces well a set of experimentally measured properties in Ti. First, we model the twin boundary structures and calculate the excess potential energies. The tilt axis for the interfaces has been chosen to be [1210] along *z* direction and boundary plane lies on *xz* plane. To calculate the interface energy, two boundaries are simulated in each modeling cell to preserve the periodicity along *y* axis, as well as *x* and *z* directions. The periodic length along *y* and *z* are 90 nm and 0.293 nm, respectively. Periodicity along the *x* direction is 1.06 nm, 0.69 nm and 1.78 nm for (1011), (1012) and (1013) STGBs, respectively. The relaxed structure and potential energy map of these three boundaries using periodic boundary conditions in all directions are shown in the Figure 2.2

In order to check the validity of implemented MEAM potential, we also compared the excess interface energies with density functional theory (DFT). DFT calculations are performed using the VASP package [34] with Projector augmented-wave potentials within the generalized gradient approximation of the exchange-correlation functional as determined by Perdew-Burke-Ernzerhof (GGA-PBE) [33]. A plane-wave cut-off energy of 300 eV is



**Figure 2.2:** Structure and potential energy (PE) per atom for three STGBs in Ti: (a)-(b)  $(\bar{1}011)$  TB, (c)-(d)  $(\bar{1}012)$ , (e)-(f)  $(\bar{1}013)$  TB. The color coding the left columns shows the potential energy of each atom. In the right column, common neighbor analysis is shown where the blue and red colors present hcp bulk and non-hcp structure indicative of the interface, respectively.

used for pure Ti. A  $14 \times 14 \times 8$  *k*-point mesh for the unit cell is well converged and it is adjusted for the supercell dimensions. This *k*-point mesh gives an energy accuracy of 1 meV atom<sup>-1</sup> for bulk Ti. Table 2.1 summarizes the GB energy for aforementioned STGBs predicted by the MEAM potential and DFT calculations and compared with the reported DFT values by Kumar *et al.* [54]. Here, we use ( $\overline{1011}$ ) and ( $\overline{1013}$ ) in the subsequent dislocation/boundary interactions.

STGB	Basal-GB misorientation	Excess $PE(\frac{mJ}{m^2})$		
		MEAM	DFT	DFT[54]
(1011)	61.52°	111.80	100.30	75.30
(1012)	42.66°	171.30	308.39	297.60
(1013)	31.56°	324.82	345.11	326.50

Table 2.1: Excess potential energy (PE) for three STGBs

For simulations of dislocation/boundary interactions, dimensions along x and y directions are chosen to be 70 nm and 60 nm, respectively. As depicted schematically in Figure 2.3, fixed boundary conditions are applied along x and y directions and periodic boundary conditions are applied along the dislocation line lying in the z direction. The cell dimension along this dislocation is 10 times the length of one periodic distance (2.9304 Å). The dislocations are introduced by displacing all the atoms according to the anisotropic displacement of the dislocation [55, 56].



**Figure 2.3:** Bicrystal cell for dislocation/boundary simulations: two grains are indicated with red and blue atomic colors, respectively. Atoms in green color are fixed in their positions during relaxation.

In the next sections, we study three different lattice dislocations:  $\langle a \rangle$  screw dislocation on {1010} prism planes,  $\langle c \rangle$  edge dislocation on {1010} prism planes and  $\langle c + a \rangle$  mixed dislocation on {1011} pyramidal-I planes, interacting with (1011) and (1013) boundaries. We also study the dislocation/boundary interaction under various shear strain components  $\gamma_{xy}$ ,  $\gamma_{xz}$  and  $\gamma_{yz}$ .

## 2.3 Twinning dislocations corresponding to (1011), (1012) and (1013) boundaries

In hcp systems, twinning dislocations are characterized by both Burgers vectors (*b*) and a step height  $h = qd_0$ , in which  $d_0$  is the unit distance between adjacent twin planes and *q* is an integer number defining the atomic layers. Previous works discussed different methods for generating the topology of twinning dislocations in Mg [49, 57, 58]. Here, we represent how to construct the twinning dislocations in different boundaries in Ti. Figure 2.4 shows the dichromatic pattern corresponding to ( $\overline{1}011$ ) and ( $\overline{1}013$ ) boundaries. Dichromatic pattern consists of lattice sites of two crystals in their twin related orientations, superimposed with the sites of one of the grains (parent grains) where the atoms coincide exactly at the interface. The set of Burgers vectors of admissible interface dislocations is the difference between translation vectors of  $t_{\mu}^2$  and  $t_{\lambda}^2$  represented in the same reference frame defined as follows:

$$\vec{b} = \vec{t_{\mu}} - \vec{t_{\lambda}} \tag{2.1}$$

Starting with a dislocation-free coherent twin boundary, we define  $\vec{t}_{\lambda}$  and  $\vec{t}_{\mu}$  translation vectors as shown in the Figure 2.4 for each boundary and with a specified step height. The right half of the coherent twin geometry is then shifted by these translation vectors on each side of the twin boundary. This creates a step and breaks the coherency. This mismatch is

restored by imposing the Burgers vector expressed in Equation 2.1. The generated defect has both dislocation and step characters.



**Figure 2.4:** Dichromatic pattern for (a) ( $\overline{1}011$ ) and (b) ( $\overline{1}013$ ) twin boundaries.  $\vec{t_{\lambda}}$  and  $\vec{t_{\mu}}$  are the translation vectors for generating the step character. Two and four step height dislocation Burgers vectors are shown in this figure. Blue and red color atoms are representative of  $\lambda$  and  $\mu$  crystallographic orientations which are mirrored about the boundary planes. Yellow colored atoms correspond to the  $\lambda$  crystallographic orientation repeated through entire cell to construct dichromatic pattern.  $\vec{b_2}$  and  $\vec{b_4}$  denote two step and four step Burgers vectors, respectively.

Analysis of the dichromatic pattern for  $(\bar{1}011)$  and  $(\bar{1}013)$  TBs show that there are two possible step heights with minimal shuffle and *b* magnitudes: q = 2 and q = 4 step height twinning dislocations. In both of the boundaries, the dislocation character of q = 2- step height is of mixed type, while that corresponding to q = 4- step height is pure edge. ( $\bar{1}012$ ) twinning dislocation (TD), however, has a q = 2- step height and a pure edge dislocation character. These TDs are shown in Figure 2.5. The line direction for these dislocations is along [ $\bar{1}2\bar{1}0$ ] zone axis. The Burgers vector components of these dislocations are listed in the Table 2.2.

Burgers vectors for the twinning dislocations explained above are given by the following equations where  $b_{t,2}$  and  $b_{t,4}$  are the 2-step and 4-step height TDs in each boundary and



**Figure 2.5:** ( $\overline{1}011$ ), ( $\overline{1}013$ ) and ( $\overline{1}012$ ) Twinning dislocations in Ti: (a),(c) 2 and 4-step height ( $\overline{1}011$ ) TB. (b),(d) 2 and 4-step height ( $\overline{1}013$ ) TB. (e) 2-step height ( $\overline{1}012$ ) TB. Color coding is the common neighbor analysis (CNA) [7]. Blue atoms have hcp coordinates while red atoms show the defective regions.

**Table 2.2:** Burgers vectors of  $(\overline{1}011)$ ,  $(\overline{1}012)$  and  $(\overline{1}013)$  twinning dislocations in Titanium (Å): Lattice parameter and c/a ratio are: a = 2.9304 Å and  $\kappa = 1.5964$ .  $\rho_e$ ,  $b_{2e}$ ,  $b_{2s}$ ,  $b_{t,2}$  and  $b_{t,4}$  are TD coefficient, 2-step edge, 2-step screw components, resultant 2-step height mixed and 4-step height pure edge Burgers vector, respectively. Sign convention in all following Burgers vector notations are right hand side start to finish convention.

	Coefficients	Burgers vector				
TB	$ ho_e$	$ b_{2e} $	$ b_{2s} $	$ b_{t,2} $	$ b_{t,4} $	
(1011)	0.0905	0.4818	1.4651	1.5423	0.9636	
(1012)	0.0813	0.5615	-	0.5615	-	
(1013)	0.0321	0.2869	1.4651	1.4930	0.5739	

 $\kappa$  is the c/a ratio. Lattice parameter and c/a ratio for Ti are: a = 2.9304 Å and  $\kappa = 1.5964$ .

$$b_{2}^{(\bar{1}011)} = b_{t,2-edge}^{(\bar{1}011)} + b_{t,2-screw}^{(\bar{1}011)} = \frac{1}{2}\rho_{e}^{(\bar{1}011)}[\bar{1}01\bar{2}] \pm \frac{1}{6}[1\bar{2}10]$$
(2.2a)

$$b_{t,4}^{(\bar{1}011)} = \rho_e^{(\bar{1}011)}[\bar{1}01\bar{2}]$$
(2.2b)

$$\rho_e^{(\bar{1}011)} = \frac{(4\kappa^2 - 9)}{(3 + 4\kappa^2)}$$
(2.2c)

$$b_{t,2}^{(\bar{1}013)} = b_{t,2-edge}^{(\bar{1}013)} + b_{t,2-screw}^{(\bar{1}013)} = \frac{1}{2}\rho_e^{(\bar{1}013)}[\bar{3}03\bar{2}] \pm \frac{1}{6}[1\bar{2}10]$$
(2.3a)

$$b_{t,4}^{(\bar{1}013)} = \rho_e^{(\bar{1}013)}[\bar{3}03\bar{2}]$$
(2.3b)

$$\rho_e^{(\bar{1}013)} = \frac{(4\kappa^2 - 9)}{(27 + 4\kappa^2)} \tag{2.3c}$$

$$b_{t,2-edge}^{(\bar{1}012)} = \rho_e^{(\bar{1}012)}[\bar{1}011]$$
(2.4a)

$$\rho_e^{(\bar{1}012)} = \frac{(3-\kappa^2)}{(\kappa^2+3)}$$
(2.4b)

### 2.4 Dislocation/boundary interactions

## 2.4.1 Interactions of the prismatic $\langle a \rangle$ screw dislocation with ( $\overline{1}011$ ) boundary

Figure 2.6(a) shows the interaction of  $\langle a \rangle$ -type screw dislocation with ( $\overline{1}011$ ) twin boundary under strain. The slip on the prismatic plane in top grain, results in nucleation of ( $\overline{1}011$ ) twin dislocations. In order to study the behavior of defects under strain, we apply incremental values of shear strain components. We find that TD with lower Peierls stress starts to move under  $\gamma_{xy} = -0.011$ . This shows that the initial  $\langle a \rangle$ -type screw dislocation dissociates into two glissile (1011) TDs on the boundary as presented in Figure 2.6(b).



**Figure 2.6:** Interactions with ( $\overline{1011}$ ) TB. (a) Glissile twinning dislocations are created on the boundary as a result of an  $\langle a \rangle$  screw dislocation. (b)  $\gamma_{xy} = -0.011$  shear strain is applied which moves the twinning dislocation. (c) presents the interaction of an  $\langle c \rangle$  prism edge dislocation with the boundary under no shear strain. (d) Applying  $\gamma_{xy} = -0.01$ ,  $\gamma_{yz} = -0.0083$  shear strains creates two twinning dislocations as well a dissociated lattice dislocation the adjacent grain. (e) depicts the  $\langle c + a \rangle$  mixed pyramidal dislocation interaction with the ( $\overline{1011}$ ) boundary with no shear strain. (f) shows that applying  $\gamma_{yz} = -0.01$  shear strain results in nucleation of a twinning dislocation and an extended lattice dislocation in the adjacent grain, similar to (d).  $b_{t,2}$ ,  $b_{st}$  and  $b_r$  are 2-step height ( $\overline{1011}$ ) TD, Shockley partial and the residual dislocation, respectively.

The Burgers vector reaction in the top grain using a Miller-Bravais [59] hexagonal crystal reference frame is given by:

$$\underbrace{\frac{1}{3}[\bar{1}2\bar{1}0](10\bar{1}0)}_{b_{(a)\,\text{screw}}} \longrightarrow \left(\underbrace{\frac{1}{2}\rho_{e}^{(\bar{1}011)}[\bar{1}01\bar{2}]}_{b_{l,2-edge}^{(\bar{1}011)}} + \underbrace{\frac{1}{6}[1\bar{2}10]}_{b_{l,2-screw}^{(\bar{1}011)}}\right)(\bar{1}011) + \left(\underbrace{-\frac{1}{2}\rho_{e}^{(\bar{1}011)}[\bar{1}01\bar{2}]}_{-b_{l,2-edge}^{(\bar{1}011)}} + \underbrace{\frac{1}{6}[1\bar{2}10]}_{b_{l,2-screw}^{(\bar{1}011)}}\right)(\bar{1}011) + \underbrace{(\underbrace{-\frac{1}{2}\rho_{e}^{(\bar{1}011)}[\bar{1}01\bar{2}]}_{-b_{l,2-edge}^{(\bar{1}011)}} + \underbrace{\frac{1}{6}[1\bar{2}10]}_{b_{l,2-screw}^{(\bar{1}011)}}\right)(\bar{1}011)$$

where the edge and screw components of the TD Burgers vectors are obtained from Equation 2.2. Two generated TDs have the same sign screw and opposite sign edge components. In the boundary cartesian reference frame shown in Figure 2.6, the above Burgers vector components are given as follows:

$$b_{\langle a \rangle \text{screw}} = a \begin{pmatrix} 0\\0\\1 \end{pmatrix} \quad , \quad b_{t,2-edge}^{(\bar{1}011)} = \frac{a}{2} \cdot \frac{4\kappa^2 - 9}{\sqrt{3 + 4\kappa^2}} \begin{pmatrix} 1\\0\\0 \end{pmatrix} \quad , \quad b_{t,2-screw}^{(\bar{1}011)} = \frac{a}{2} \begin{pmatrix} 0\\0\\1 \end{pmatrix}$$

where *a* and  $\kappa$  represent the lattice constant and c/a ratio and  $b_{t,2-edge}^{(\bar{1}011)}$  and  $b_{t,2-screw}^{(\bar{1}011)}$  indicate the 2-step height edge and screw components, respectively.

### 2.4.2 Interactions of the prismatic $\langle c \rangle$ edge and pyramidal mixed $\langle c + a \rangle$ dislocations with ( $\overline{1}011$ ) boundary

In this section, we study the interaction between an edge  $\langle c \rangle$  on {1010} prism planes and mixed  $\langle c + a \rangle$  on {1011} pyramidal-I planes and the (1011) boundary. Figure 2.6(c) shows the former interaction. Applying two shear components of  $\gamma_{xy} = -0.01$  and  $\gamma_{yz} = -0.0083$  leads to further dislocation reactions, creating three types of reaction products as shown in Figure 2.6(d). These products include two {1011} TDs, which have opposite signs Burgers vectors and move in opposite directions under applied strain, a partial dislocation entering the second grain and a residual sessile dislocation on the boundary. Color code in the figure

shows the common neighbor analysis featured in Ovito [7]. The partial dislocation in the second grain is leaving behind a basal stacking fault, suggesting a basal dissociation of an  $\langle a \rangle$ -type dislocation. We analyze the nucleated  $\langle a \rangle$  dislocation in more detail, to determine its Burgers vector direction and deduce the entire dislocation reaction at the boundary.

Figure 2.7 shows that the trailing partial is located at the boundary which makes it difficult to identify the character of residual component on the boundary. The leading partial, however, passes through the boundary and could be analyzed. Given that the line direction is fixed, the nucleated  $\langle a \rangle$  dislocation could either be of mixed or screw characters as shown in Figure 2.8. The mixed dislocation (AC or BC) dissociates into  $A\delta$  and  $\delta C$  or  $B\delta$  and  $\delta C$  partials. In both cases, the  $\delta C$  partial has a pure edge character. On the other hand, if the  $\langle a \rangle$  dislocation has a screw character (AB), the resulting Shockley partials would be  $A\delta$  and  $\delta B$ , both of which are mixed dislocations. We then analyzed the character of the leading partial using Nye tensor analysis [60]. The result of this analysis which is shown in the Figure 2.8(c)-(f) indicates that the leading partial is of pure edge character ( $\delta C$ ), thus revealing that the nucleated  $\langle a \rangle$  must be of mixed type (either AC or BC). Therefore, the Burgers vector reaction of a  $\langle c \rangle$  edge interacting with ( $\overline{1011}$ ) boundary would be:

$$\underbrace{[0001](10\bar{1}0)}_{b_{(c) \text{ edge}}} \longrightarrow b_{t,2-1}^{(\bar{1}011)} + b_{t,2-2}^{(\bar{1}011)} + b_{st,mixed} + b_{st,edge} + b_r$$

In the boundary cartesian reference frame, each of the reaction components in the above equations are given by:

$$b_{\langle c \rangle edge} = \frac{a \cdot \kappa}{\sqrt{3} + 4\kappa^2} \begin{pmatrix} -2\kappa \\ -\sqrt{3} \\ 0 \end{pmatrix} , \quad b_{t,2-1}^{(\bar{1}011)} = \frac{a}{2} \begin{pmatrix} \frac{4\kappa^2 - 9}{\sqrt{3} + 4\kappa^2} \\ 0 \\ 1 \end{pmatrix} , \quad b_{t,2-2}^{(\bar{1}011)} = \frac{a}{2} \begin{pmatrix} -\frac{4\kappa^2 - 9}{\sqrt{3} + 4\kappa^2} \\ 0 \\ -1 \end{pmatrix} \\ \text{AC dissociation: } b_{st,mixed}^{(\bar{1}011)} = \frac{a}{\sqrt{3}} \begin{pmatrix} -\frac{\sqrt{3}}{2\sqrt{4\kappa^2 + 3}} \\ -\frac{\sqrt{3}}{2\sqrt{4\kappa^2 + 3}} \\ \frac{\sqrt{3}}{2} \end{pmatrix} , \quad b_{st,edge}^{(\bar{1}011)} = \frac{a}{\sqrt{3}} \begin{pmatrix} -\frac{\sqrt{3}}{\sqrt{4\kappa^2 + 3}} \\ -\frac{\sqrt{3}}{2\sqrt{4\kappa^2 + 3}} \\ 0 \end{pmatrix} \\ \text{BC dissociation: } b_{st,mixed}^{(\bar{1}011)} = \frac{a}{\sqrt{3}} \begin{pmatrix} -\frac{\sqrt{3}}{2\sqrt{4\kappa^2 + 3}} \\ -\frac{\sqrt{3}}{2\sqrt{4\kappa^2 + 3}} \\ -\frac{\sqrt{3}}{2} \end{pmatrix} , \quad b_{st,edge}^{(\bar{1}011)} = \frac{a}{\sqrt{3}} \begin{pmatrix} -\frac{\sqrt{3}}{\sqrt{4\kappa^2 + 3}} \\ -\frac{\sqrt{3}}{2\sqrt{4\kappa^2 + 3}} \\ -\frac{\sqrt{3}}{2\sqrt{4\kappa^2 + 3}} \\ 0 \end{pmatrix} \\ \end{array}$$

Similar behavior is also observed as a result of the pyramidal-I mixed  $\langle c + a \rangle$  interaction with ( $\overline{1}011$ ) boundary. Figure 2.6(e) shows this interaction. During this interaction, a glissile ( $\overline{1}011$ ) TD, a Shockely partial trailed by a basal stacking fault in the second grain, and a sessile residual component at the boundary are formed. Note that unlike in case of the  $\langle c \rangle$  dislocation, this reaction occurs even in the absence of applied strain. Figure 2.6(f) shows the  $\langle c + a \rangle$  dislocation interaction with the ( $\overline{1}011$ ) GB under  $\gamma_{yz} = -0.01$  shear strain where the TD glides under strain. The dislocation reaction is given by:

$$\underbrace{-\frac{1}{3}[2\bar{1}\bar{1}3](\bar{1}011)}_{b_{(c+a)\text{ mixed}}} \longrightarrow b_{t,2}^{(\bar{1}011)} + b_{st,mixed} + b_{st,edge} + b_r$$

where, in boundary cartesian reference frame:

$$b_{\langle c+a\rangle\text{mixed}} = \frac{a}{2} \begin{pmatrix} -\sqrt{3}+4\kappa^2 \\ 0 \\ -1 \end{pmatrix} , \quad b_{i,2}^{(\bar{1}011)} = \frac{a}{2} \begin{pmatrix} -\frac{4\kappa^2-9}{\sqrt{3}+4\kappa^2} \\ 0 \\ -1 \end{pmatrix} , \quad b_{st,mixed}^{(\bar{1}011)} = \frac{a}{\sqrt{3}} \begin{pmatrix} -\frac{\sqrt{3}}{2\sqrt{4\kappa^2+3}} \\ -\frac{\kappa}{\sqrt{3}} \\ \frac{\sqrt{3}}{2} \end{pmatrix} \\ b_{st,edge}^{(\bar{1}011)} = \frac{a}{\sqrt{3}} \begin{pmatrix} -\frac{\sqrt{3}}{\sqrt{4\kappa^2+3}} \\ -\frac{\sqrt{3}}{\sqrt{4\kappa^2+3}} \\ -\frac{\sqrt{3}}{\sqrt{4\kappa^2+3}} \\ 0 \end{pmatrix}.$$

In the above equations,  $b_{t,2}^{(\bar{1}011)}$ ,  $b_{st,mixed}$ ,  $b_{st,edge}$  and  $b_r$  are the Burgers vectors for 2-step height ( $\bar{1}011$ ) TD, the mixed type Shockley partial, the edge type Shockley partial and the residual dislocation, respectively.



**Figure 2.7:** Nye tensor analysis on the partial dislocations corresponding to the stacking fault in the second grain: (a)  $\langle c \rangle$  prism edge (b)  $\langle c + a \rangle$  pyramidal mixed dislocation interactions with (1011) STGB. Edge components (c)-(d) and Screw components (e)-(f) of the partial dislocation which is passed through the boundary is plotted for  $\langle c \rangle$  and  $\langle c + a \rangle$  dislocations, respectively. This shows that for both cases, the leading partials is pure edge, suggesting the nucleated  $\langle a \rangle$  dislocation must be of mixed type.



**Figure 2.8:** Possible dissociation scenarios for an  $\langle a \rangle$  dislocation on basal planes. In all of our dislocation/boundary interaction simulations, line direction is fixed and is chosen along [1210]. Burgers vector AB corresponds to a screw dislocation, while Burgers vectors AC or BC correspond to mixed type dislocations. Further analysis of possible Shockley partial Burgers vectors reveal that only  $\delta C$  is of pure edge character. This partial dislocation can only be created by dissociation of a mixed  $\langle a \rangle$  dislocation, i.e. AC or BC.

### 2.4.3 Interactions of the prismatic (a) screw dislocation with (1013) boundary

Figure 2.9 shows the interaction of prismatic screw  $\langle a \rangle$  dislocation and (1013) boundary. Without applying any strain, the screw  $\langle a \rangle$  dislocation creates 2-step and 4-step height (1013) TDs on the boundary. Figure 2.9(b) and (c) show the evolution of defects under  $\gamma_{yz} = -0.016$  and  $\gamma_{yz} = -0.018$  shear strains, respectively. All of the nucleated TDs are glissile and move under the shear strain. The Burgers vector reaction for this interaction, in both hexagonal and boundary cartesian reference frames, is given by:

$$\gamma_{yz} = -0.0157: \underbrace{\frac{1}{3}[\bar{1}2\bar{1}0](\bar{1}013)}_{b_{(a)\ screw}} \longrightarrow 2 \times \left(\underbrace{b_{t,2-edge}^{(\bar{1}013)} + b_{t,2-screw}^{(\bar{1}013)}}_{b_{t,2}^{(\bar{1}013)}}\right) - b_{t,4}^{(\bar{1}013)}$$

$$b_{\langle a \rangle \text{screw}} = a \begin{pmatrix} 0\\0\\1 \end{pmatrix} \quad , \quad b_{t,2}^{(\bar{1}013)} = \frac{a}{2} \begin{pmatrix} \frac{4\kappa^2 - 9}{\sqrt{27 + 4\kappa^2}}\\0\\1 \end{pmatrix} \quad , \quad b_{t,4}^{(\bar{1}013)} = a \begin{pmatrix} \frac{4\kappa^2 - 9}{\sqrt{27 + 4\kappa^2}}\\0\\0 \end{pmatrix}$$

$$\gamma_{yz} = 0 \text{ and } \gamma_{yz} = -0.01789 : \underbrace{\frac{1}{3} [\bar{1}2\bar{1}0](\bar{1}013)}_{b_{\langle a \rangle \text{ screw}}} \longrightarrow \underbrace{\left(\underbrace{b_{t,2-edge}^{(\bar{1}013)} + b_{t,2-screw}^{(\bar{1}013)}}_{b_{\langle z-1}^{(\bar{1}013)}}\right) + \left(-\underbrace{b_{t,2-edge}^{(\bar{1}013)} + b_{t,2-screw}^{(\bar{1}013)}}_{b_{\langle z-2}^{(\bar{1}013)}}\right)$$

$$b_{\langle a \rangle \text{screw}} = a \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad , \quad b_{t,2-1}^{(\bar{1}013)} = \frac{a}{2} \begin{pmatrix} \frac{4\kappa^2 - 9}{\sqrt{27 + 4\kappa^2}} \\ 0 \\ 1 \end{pmatrix} \quad , \quad b_{t,2-2}^{(\bar{1}013)} = \frac{a}{2} \begin{pmatrix} -\frac{4\kappa^2 - 9}{\sqrt{27 + 4\kappa^2}} \\ 0 \\ 1 \end{pmatrix}$$

where  $b_{t,2-edge}^{(1013)}$  and  $b_{t,2-screw}^{(1013)}$  are edge and screw components of 2-step height (1013) TD, respectively. The above reactions show that there is no residual sessile dislocation remaining on the boundary.

These simulations show that as the shear strain increases, 4-step height TDs with opposite Burgers vectors are formed more frequently (cf. Figure 2.9(c) ). These type of twinning dislocations are marked by defective regions on the twin boundary in the form of "islands" and "zigzags". The term "island" refers to the dislocation-free shifted part of the boundary in between two opposite sign Burgers vectors. "zigzag" kinks are formed when two dislocations with opposite sign Burgers Vectors meet at the same point. We check the stability of these zigzag kinks and islands in separate simulations. Two 4-step height ( $\overline{1013}$ ) TDs with opposite signs Burgers vectors are applied to the ( $\overline{1013}$ ) GB at three atomic distance from each other. The relaxed geometry of these structures are shown in the Figure 2.10 and confirms that the zigzag and islands on the ( $\overline{1013}$ ) boundary are both stable. Figure 2.11 shows that under the shear strain of  $\gamma_{xy} = -0.007$ , two opposite sign TDs move apart from each other.



**Figure 2.9:** Interaction of  $\langle a \rangle$  dislocation with ( $\bar{1}013$ ) TB. (a) Shows the relaxed geometry after the dislocation is introduced at the boundary under zero strain. The interaction results in two 4-step height and 2-step height TDs. (b) Shows the relaxed cell under  $\gamma_{yz} = -0.016$  shear strain resulting in the TDs to move. (c) Shows the configurations of defects at  $\gamma_{yz} = -0.018$ . By increasing the shear strain, zigzag kinks are formed. Note that the net Burgers vector content of these defects is zero. Black atom is highlighted to be used as a reference. *S*, *b*<sub>t,2</sub> and *b*<sub>t,4</sub> show [ $\bar{1}2\bar{1}0$ ] screw dislocation, 2-step and 4-step height ( $\bar{1}013$ ) TDs, respectively.

## 2.4.4 Interactions of the pyramidal $\langle c+a\rangle$ dislocation with $(\bar{1}013)$ boundary

In this section, we study the interaction of a  $\langle c + a \rangle$  mixed type dislocation on the pyramidal-I plane with the ( $\overline{1}013$ ) boundary. Figure 2.12(a) shows the relaxed structure under no applied shear strain where a defective region is nucleated in the neighboring grain. We applied various components of shear strain in combination to analyze the nucleated defects. Figure 2.12(b)-(d) show the geometry under the effect of two shear strain



**Figure 2.10:** Formation of zigzag kinks on ( $\overline{1013}$ ). Two opposite sign pure edge 4-step height ( $\overline{1013}$ ) form a stable zigzag. (a) Shows the relaxed ( $\overline{1013}$ ) zigzag, which is a stable configuration. (b) Shows the relaxed stable island which consists of two opposite sign 4-step height ( $\overline{1013}$ ) TDs.

components  $\gamma_{xy} = -0.005$ ,  $\gamma_{yz} = -0.027$  after 400, 700 and 1300 relaxation steps, respectively. As it is shown, the defective nucleus in the second grain grows as the shear applied. The misorientation angle between inside and outside of the nucleus region is approximately 42.66°, which matches that of a ( $\overline{1012}$ ) twin boundary (cf. Table 2.1 ), confirming that the defective region is in fact a ( $\overline{1012}$ ) twin nucleus. More in-depth analysis of the boundary of this defect also shows that the generated nucleus is bounded by Basal-to-Prismatic (BP) boundaries, which are extensively observed during the growth of ( $\overline{1012}$ ) twins in hcp systems [61]. BP facets show abrupt changes in the orientation from the prismatic plane in one grain to the basal plane in the other grain. This interaction marks a possible ( $\overline{1012}$ )



**Figure 2.11:**  $\gamma_{xy} = -0.007$  shear strain applied on ( $\overline{1}013$ ) 4-step island. Figures are snapshots of the simulation after: (a) 0, (b) 200 and (c) 550 relaxation steps, respectively. Note that the right 4-step height dislocation in (a) moves in the [ $\overline{3}03\overline{2}$ ] direction. The kinks formed in (b) move in the opposite directions. Green and purple dots are to be used as a reference.

twin nucleation mechanism as a result of  $\langle c + a \rangle$  dislocation interactions with grain boundaries. Other reaction products include two "zigzag" structures– 4-step height ( $\bar{1}013$ ) TDs with opposite Burgers vectors– and a 2-step height ( $\bar{1}013$ ) TD. The dissociation reaction for mixed  $\langle c + a \rangle$  dislocation at the ( $\bar{1}013$ ) boundary is given by:

$$\underbrace{-\frac{1}{3}[2\bar{1}\bar{1}3](\bar{1}013)}_{b_{(c+a) \text{ mixed}}} \longrightarrow b_{t,2-1}^{(\bar{1}013)} + b_{t,2-2}^{(\bar{1}013)} + b_{t,2}^{(\bar{1}012)} + b_r$$

where

$$b_{\langle c+a\rangle \text{ mixed}} = \frac{a}{2} \begin{pmatrix} -\frac{9+4\kappa^2}{\sqrt{27+4\kappa^2}} \\ \frac{4\sqrt{3\kappa}}{\sqrt{27+4\kappa^2}} \\ -1 \end{pmatrix}, \quad b_{t,2-1}^{(\bar{1}013)} = \frac{a}{2} \begin{pmatrix} \frac{4\kappa^2-9}{\sqrt{27+4\kappa^2}} \\ 0 \\ 1 \end{pmatrix}, \quad b_{t,2-2}^{(\bar{1}013)} = \frac{a}{2} \begin{pmatrix} -\frac{4\kappa^2-9}{\sqrt{27+4\kappa^2}} \\ 0 \\ -1 \end{pmatrix} \\ b_{t,2}^{[10\bar{1}\bar{1}](\bar{1}012)} = \frac{a}{2} \frac{3-\kappa^2}{\kappa^2+3} \begin{pmatrix} \frac{-18+4\kappa^2}{\sqrt{27+4\kappa^2}} \\ -\frac{10\sqrt{3\kappa}}{\sqrt{27+4\kappa^2}} \\ 0 \end{pmatrix}$$

and  $b_{t,2}^{(\bar{1}013)}$ ,  $b_{t,2}^{(\bar{1}012)}$  and  $b_r$  are 2-step height ( $\bar{1}013$ ), ( $\bar{1}012$ ) and residual component remained on the boundary, respectively.

## 2.4.5 Interactions of the prismatic edge $\langle c \rangle$ dislocation with $(\bar{1}013)$ boundary

Next, we study the interaction of prismatic edge  $\langle c \rangle$  dislocation with ( $\bar{1}013$ ) boundary. Figure 2.13(a) shows the relaxed structure under no shear strain. In the absence of applied strain, a ( $\bar{1}012$ ) twin embryo nucleates as a result of this interaction. This is another source for ( $\bar{1}012$ ) twin nucleation. In addition, two 4- step height ( $\bar{1}013$ ) TDs are formed on the right and left side of twin embryo. Upon applying the shear strain of  $\gamma_{yz} = -0.03$ , additional defects are nucleated as shown in the Figure 2.13(b), and in more detail, in Figure 2.13(c)-(f). Two 2-step height ( $\bar{1}013$ ) TDs are formed on the right side of the ( $\bar{1}012$ ) twin embryo. In addition, 4-step height ( $\bar{1}013$ ) kinks as well as ( $\bar{1}013$ ) island and simple 2 and 4-step height TDs are nucleated on the left side of the twin embryo. Besides the above reaction products, an  $\langle a \rangle$ -type dislocation is also nucleated, similar to the one observed in the interactions with ( $\bar{1}011$ ) boundary explained in Section 2.4.2. This dislocation glides on the basal planes of the second grain under the applied strain. In order to determine the character of this dislocation and consequently the vector representation of Burgers vector, Nye tensor analysis is performed. The edge and screw components of the Nye tensor distribution, presented in Figure 2.14, clearly show that the dislocation dissociates into



**Figure 2.12:**  $\langle c+a \rangle$  dislocation interaction with ( $\overline{1}013$ ) TB. (a) Depicts the relaxed geometry under no applied strain. A defective region is nucleated in the neighboring grain. (b)-(d) Show the geometry under simultaneous application of  $\gamma_{xy} = -0.005$ ,  $\gamma_{yz} = -0.027$  after 400, 700 and 1300 relaxation steps, respectively. 2, 4-step height TDs, 4-step ( $\overline{1}013$ ) zigzags are formed on the boundary and ( $\overline{1}012$ ) twinning is nucleated in the other grain. Twin nucleus is bounded by { $\overline{1}012$ } as well as basal-prismatic facets.  $b_{pyr}$ ,  $b_{t,2}$ ,  $b_{t,4}$  and  $b_{t,\overline{1}012}$  show  $\langle c+a \rangle$  mixed, 2-step, 4-step height ( $\overline{1}013$ ) twinning and ( $\overline{1}012$ ) twinning dislocations, respectively.

two partials with identical screw components and equal and opposite edge components. Referring back to the Figure 2.8 reveals that the dissociated partials of this case are  $A\delta$  and  $\delta B$ . This suggests that the nucleated  $\langle a \rangle$  dislocation has the screw character. The dislocation reaction follows the equations below:

$$\underbrace{[0001](10\bar{1}0)}_{b_{(c) \text{ edge}}} \longrightarrow \left(\underbrace{2b_{t,2-1}^{(\bar{1}013)} + b_{t,4-1}^{(\bar{1}013)}}_{\text{right side of embryo}}\right) + \left(\underbrace{b_{t,2-2}^{(\bar{1}013)} + 2b_{t,4-2}^{(\bar{1}013)}}_{\text{left side of embryo}}\right) + b_{st} + b_{t,2}^{(\bar{1}012)} + b_{r}$$

where

$$b_{\langle c \rangle \text{edge}} = \frac{a \cdot \kappa}{\sqrt{27 + 4\kappa^2}} \begin{pmatrix} -2\kappa \\ -3\sqrt{3} \\ 0 \end{pmatrix} , \quad b_{t,2-1}^{(\bar{1}013)} : \frac{a}{2} \begin{pmatrix} \frac{4\kappa^2 - 9}{\sqrt{27 + 4\kappa^2}} \\ 0 \\ 1 \end{pmatrix} , \quad b_{t,2-2}^{(\bar{1}013)} = \frac{a}{2} \begin{pmatrix} -\frac{4\kappa^2 - 9}{\sqrt{27 + 4\kappa^2}} \\ 0 \\ -1 \end{pmatrix} \\ b_{t,4-1}^{(\bar{1}013)} = a \begin{pmatrix} \frac{4\kappa^2 - 9}{\sqrt{27 + 4\kappa^2}} \\ 0 \\ 0 \end{pmatrix} , \quad b_{t,4-2}^{(\bar{1}013)} = a \begin{pmatrix} -\frac{4\kappa^2 - 9}{\sqrt{27 + 4\kappa^2}} \\ 0 \\ 0 \end{pmatrix} \end{pmatrix} , \quad b_{st}^{(\bar{1}013)} = \frac{a}{\sqrt{3}} \begin{pmatrix} -\frac{3\sqrt{3}}{2\sqrt{27 + 4\kappa^2}} \\ -\frac{\kappa}{\sqrt{27 + 4\kappa^2}} \\ \frac{\sqrt{3}}{2} \end{pmatrix} \\ b_{t,2}^{[\bar{1}01\bar{1}](\bar{1}012)} : \frac{a}{2} \cdot \frac{3-\kappa^2}{\kappa^2 + 3} \begin{pmatrix} \frac{18 + 4\kappa^2}{\sqrt{27 + 4\kappa^2}} \\ -\frac{2\sqrt{3\kappa}}{\sqrt{27 + 4\kappa^2}} \\ 0 \end{pmatrix} \\ \text{and } b_{t,2}^{(\bar{1}013)}, \quad b_{t,4}^{(\bar{1}013)}, \quad b_{st}^{(\bar{1}012)}, \quad b_{st} \text{ and } b_r \text{ in above equations are 2-step, 4-step height (\bar{1}013), \end{cases}$$

 $(\bar{1}012)$  TD, stacking fault and residual dislocation on the boundary, respectively.

### 2.5 Concluding Remarks

In this chapter, we studied the interaction of three dislocation systems, with two symmetric tilt (twin) boundaries in Ti using atomistic simulations. The results reveal new mechanisms of twin nucleation and growth as a result of these interactions. In both cases of ( $\overline{1011}$ ) and ( $\overline{1013}$ ), screw  $\langle a \rangle$ -type dislocation generates the corresponding twinning



**Figure 2.13:** Prismatic edge  $\langle c \rangle$  dislocation interaction with the ( $\bar{1}013$ ) boundary. (a) Relaxed geometry is shown under no applied strain. A well-defined ( $\bar{1}012$ ) twin embryo is nucleated in the neighboring grain (b) Additional defects are created upon application of  $\gamma_{yz} = -0.03$  shear strain. The insets in (c)-(f) provide a closer look at these defects as follows. (c) 2-step height ( $\bar{1}013$ ) TD, (d)-(e) ( $\bar{1}012$ ) twin embryo and a dissociated basal dislocation in the second grain and (f) 2-step, 4-step height and zigzag kinks on the boundary. Basal-Prism facet as well as ( $\bar{1}012$ ) TD is represented on the twin embryo.  $b_{edge}$ ,  $b_{t,2}$ ,  $b_{t,4}$ ,  $b_{t,\bar{1}012}$  and BP show  $\langle c \rangle$  edge, 2-step, 4-step height ( $\bar{1}013$ ) twinning, ( $\bar{1}012$ ) twinning dislocations and Basal-Prism interface, respectively.

dislocations on each boundary. Nucleation of TDs on ( $\overline{1}011$ ) twin boundary, from an impingement of  $\langle a \rangle$  type screw dislocation, is consistent with earlier atomistic simulations of



**Figure 2.14:** Nye tensor analysis on the basal dislocation, nucleated from the interaction of a prismatic  $\langle c \rangle$  edge dislocation with the ( $\overline{1}013$ ) boundary. (a) Shows a section of Figure 2.13. The dissociated dislocation is magnified in (b) and reoriented such that basal planes are aligned horizontally. Edge and screw components are shown in (c) and (d), respectively. The partial dislocations have the same edge component, with opposite signs, and the same sign screw component. The Nye tensor analysis shows that both partials are mixed type dislocations, suggesting that the original  $\langle a \rangle$  type dislocation must have been of screw character.

Serra and Bacon in model hcp systems [45] and experimental observations of dislocation interaction with twin boundaries [51].

New TDs are generated on both ( $\overline{1}011$ ) and ( $\overline{1}013$ ) twin boundaries as a result of  $\langle c \rangle$ and  $\langle c + a \rangle$  dislocations. The interaction of these dislocations with ( $\overline{1}011$ ) boundary lead to the  $\langle a \rangle$  type slip on the basal planes in the neighboring grain. In case of the ( $\overline{1}013$ ) twin boundary, ( $10\overline{1}2$ ) twin embryo has been nucleated in the adjacent grain. This embryo grows as the applied shear strain increases. This nucleation mechanism implies that ( $10\overline{1}2$ ) twinning can be enhanced as a result of  $\langle c \rangle$  and  $\langle c + a \rangle$  slip, complementing previous studies suggesting the possibility of  $(10\overline{1}2)$  twin nucleation from  $\langle c \rangle$  and  $\langle c + a \rangle$  lattice dislocations [62]. The framework proposed in this study can be applied to investigate any type of dislocation/symmetrical tilt grain boundaries interaction in Ti within a systematic approach.

### Chapter 3: Slip-induced twinning from general (random) grain boundaries in titanium

Slip transfer through grain boundaries plays an important role on heterogeneous deformation of polycrystalline materials. It is experimentally observed that dislocation slip in soft-oriented grain (off *c*-axis loading) can stimulate twin nucleation in the adjacent hard-oriented grain (*c*-axis loading) when the slip and twinning systems are well-aligned. Alignment can be described by Luster-Morris parameter m', which depends on the angle between loading and the slip direction as well as the angle between Burgers vectors of the slip and twinning systems. Although high m' values frequently correlate with twin nucleation in soft/hard grain pairs, there are some outlier cases in which a high m' does not lead to twin nucleation. In this study, we simulate such grain pairs using molecular dynamics simulations at 0 K and analyze the slip transfer through the grain boundary. Generated defects as a result of dislocation/random grain boundary interactions are then analyzed. The methods used to simulate and analyze the general grain pairs, random grain boundaries and the generated defects are discussed. Good agreement between computational results and experimental observations leads to new insights on the nucleation of various defects from a random grain boundary in Ti.

#### 3.1 Introduction

Titanium and its alloys have been widely used in structural applications. However, knowledge of the microstructure evolution during plastic deformation is still unclear. The primary slip mode in hexagonal Ti is  $\{10\overline{1}0\}\langle 1\overline{2}10\rangle$  prismatic slip. While the critical resolved shear stress for prismatic slip is lower than other slip modes, ductile deformation requires at least five active independent slip systems based on the von Mises criterion [16]. As a result, nonprismatic slip modes such as  $\{10\overline{1}1\}\langle 11\overline{2}\overline{3}\rangle$  first-order pyramidal  $\langle c + a \rangle$ ,  $\{2\overline{1}\overline{1}2\}\langle 2\overline{1}\overline{1}\overline{3}\rangle$  second-order pyramidal  $\langle c + a \rangle$  and deformation twinning such as  $\{10\overline{1}2\}\langle \overline{1}011\rangle$  are necessary to accommodate ductile plastic deformation. The plastic anisotropy in hcp Ti results in heterogeneous deformation among the grains of a polycrystal. The plastic activity of each grain within a polycrystalline material can in fact affect the deformation of surrounding grains. As a results, different orientations may develop within a given grain.

A comprehensive understanding of the plastic deformation of grains is strongly dependent on the structure and properties of grain boundaries (GB) between the grain pairs. GBs are the microstructural features of polycrystalline materials which impact the bulk properties [63]. GBs can act as sinks and/or sources of defects such as vacancies, interstitials and dislocations [64]. Interaction of dislocations and grain boundaries can lower the energy of boundary by decomposing the initial dislocation to the partials with smaller Burgers vectors at the boundary or in adjacent grain. This may lead to the structure change in a given boundary and needs to be taken into account in plastic deformation analysis. The character of GBs also influence plasticity in the two adjacent grains. As a result, quantitative analysis of GB structures and slip transfer across the boundaries is crucial in understanding the mechanisms behind the plastic deformation of materials. The aim of this chapter is to quantify the role of strain transfer in the activation of non-prismatic slip and deformation twinning in  $\alpha$ -Ti. It is experimentally observed that dislocation slip in soft-oriented grain (off *c*-axis loading) can stimulate twin nucleation in the neighboring hard grain (*c*-axis loading) when the slip and twinning systems are well aligned. While the good alignment and high Schmid factor have been found to be the necessary conditions for twinning to be activated in the nearing grain, some outlier cases identified where the slip-stimulated twin has not been observed. Here, we investigate the role of these factors and the stress/strain states on the slip-stimulated twinning by modeling the random grain boundaries and analyzing the slip transfer through the interfaces. To this end, the criterion for slip-stimulated twinning based on previous experimental observations are discussed in Section 3.2. Then, the characterization results performed by our experimental collaborators in the Michael Mills'lab at OSU are presented. In Section 3.3, the details of atomistic simulations of the dislocation interaction with the random grain boundaries are presented. Simulation results are discussed in Section 3.4. A summary of our findings is given in section Section 3.5.

#### **3.2** Slip transfer and experimental analysis

The quantitative study of slip transfer through the grain boundaries has been extensively explored in the literature [65, 66, 67, 68]. Luster and Morris [8] showed that slip transfer could be predicted when the product  $m' = \cos \kappa \cos \psi$ , named as Luster-Morris parameter, is maximized.  $\kappa$  and  $\psi$  are the angles between slip vectors and the angle between slip plane normals of two adjacent grains, respectively. In the case of slip-induced twinning, the m' parameter is governed by the alignment between dislocation and twinning Burgers vectors in soft/hard grain and the angle between the active slip and the operating twinning planes in

the soft/hard grains. This factor is able to predict the experimentally observed slip transfer using transmission electron microscope (TEM) and also is applicable to the cases where variable slip plane (cross-slip) near the boundary is possible [67, 68, 69]. The other integral part in slip transfer is the importance of resolved shear stress (RSS) on the outgoing system. The combination of these two factors have been proposed to be the predictive criterion for slip transfer through interfaces.

Previously, researchers at Michigan State University (MSU) showed that m' can be used as a potential predictive parameter for slip-stimulated twin nucleation [8]. Figure 3.1 shows the distribution of m' and  $m_t$  (the Schmid factor for twinning) in the characterized experimental samples. The S+T label corresponds to the cases where slip in one grain nucleated twinning in the adjacent grain and S+O shows the cases where slip in the soft grain did not trigger twinning in the neighboring hard grain. In most of the cases, grain pairs with a combination of high m' and  $m_t$  were more likely to exhibit slip-stimulated twin nucleation, with m' being the more important parameter. However, some interesting outlier cases were observed with apparently favorable m' and  $m_t$  values which did not exhibit twinning. The observations reported in the work of Wang *et al.* highlights the fact that atomic-scale mechanisms, due to the geometry and crystallographic orientation of the specific grains and interface between them, most likely play an important role in the twin nucleation mechanisms.

In collaboration with MSU, our colleagues in the Mills group characterized these samples of high purity Ti [9]. Figure 3.2 shows the scanning electron microscope (SEM) level analysis corresponding to one of the outlier cases. Slip trace analysis revealed that prismatic slip bands are observed in the soft oriented grain 1 (G1).  $[11\overline{2}0](1\overline{1}01)$  pyramidal slip was observed as the active deformation mode in the grain 2 (G2). No twin activity



**Figure 3.1:** Correlation of a large number of slip transmission (S), twinning (T) and no event (0) as a function of Schmid factor for twinning  $(m_t)$  and Morris and Luster slip transmission parameter (m'). Outlier cases are indicated with red circles. (Adapted from [8])

has been identified in the G2. Next, pole figure analysis is implemented to characterize the crystallographic orientation of the grains and the GB. Grain normal, interface and GB plane normal directions have been measured experimentally as illustrated in Figure 3.3. These values provide direct information about the five macroscopic degrees of freedom required to define a random grain boundary.

In the next section, we model the presented outlier grain pair and the interconnecting random grain boundary using atomistic simulations. Modeling dislocation/random grain boundary interactions would pave the way to understanding the underlying mechanism responsible for the deformation modes observed in the experiments.



**Figure 3.2:** SEM-level analysis by Mills group at OSU [9] of an outlier case where slip in grain 1 initiated pyramidal slip in grain 2 with no twin activity observed.

### 3.3 Computational method

We use LAMMPS [52] software to perform 0 K energy minimization. A modified embedded atom method potential (MEAM) developed by Hennig *et al.* [53] is used throughout the simulations. This potential has been shown to reproduce well a set of experimentally measured properties in Ti. The bicrystal used in this simulation setup is comprised of two grains oriented in different crystal orientations measured experimentally and stacked together according to the GB normal direction. Figure 3.3 schematically shows the bicrystal which is used to model the outlier case. Fixed boundary condition is incorporated along all directions. Atoms within the range of 20 Å from edges of the cell have been fixed in displacement in all directions according to the implemented MEAM potential cut-off. We set our reference to the Miller-Bravais [59] hexagonal crystal reference frame of the upper hard grain (G2) to present the crystallographic directions and plane normals. The GB
normal direction for the outlier case is set along *Z*:  $[\bar{1}\bar{4}52]$  measured from experimental analysis. GB lies on *XY*, where  $[\bar{7}341]$  crystallographic direction is along *Y*.



**Figure 3.3:** Bicrystal setup in MD simulations sliced along *Y*. The grain orientations and grain boundary plane indicated in this figure are chosen based on the experimental measurements. Blue and red color shows the inner cube with free atoms and outer layer with 20 Å thickness of fixed atoms in all directions, respectively.

First, we perform size test analyses to find the sufficiently large cell dimensions for the simulations. We start with a cubic grain shape of 50 Å side length for both grains and increase it up to 800 Å. We measure  $E_{GB}$ , the excess grain boundary energy, by subtracting the potential energy of each atom in the bicrystal from the bulk supercell with the same number of atoms divided by the grain boundary area. Figure 3.4(a) shows the excess grain boundary energy of the bicrystal with different sizes. As it is shown, grain boundary energy of the cell with 400 Å side length size lies within the 0.3% of converged value of 729.8 mJ/m<sup>2</sup> and therefore we proceed with this cell dimension in the next steps.

Next, we need to investigate the effect of microscopic degrees of freedom (DOF) on the grain boundary energy. This leads to finding the metastable configurations where the local grain boundary energy minima occur. Microscopic DOF can be examined through the rigid-body displacement of two adjoining crystals with respect to each other. This type of displacements have three components,  $t_1$  and  $t_2$  and  $t_3$  (known as *t*-space [64]) where  $t_1$  and  $t_2$  lie within the GB plane and  $t_3$  perpendicular to the GB plane. As the  $t_3$  component is defined uniquely from the GB macroscopic DOF energy minimization, microscopic DOF would be reduced to  $t = (t_1, t_2)$ . Figure 3.4(b) schematically shows the *t*-space displacements. To find the minimum energy configuration associated with the microscopic DOF in our model, two grains are displaced within the range of 0 - 10 Å with respect to each other in both X and Y directions and excess grain boundary energy for each configuration is calculated. Figure 3.5 shows the contour plot of energy map as a function of 2D displacement of grains. These calculations show the local minimum GB energy corresponds to the grain displacement of (3.5, 9) Å on XY GB plane.



**Figure 3.4:** Grain boundary structure optimization. (a) Shows the excess grain boundary energy of bicrystal with different cell dimensions. (b) Shows the microscopic degrees of freedom associated with the grain boundary structure known as *t*-space.



**Figure 3.5:** The effect of microscopic degrees of freedom on GB excess energy. (a) and (b) Show the 3D and the cross section of energy map constructed by sliding top grain with respect to the lower grain, respectively.

After finding the minimum energy GB structure, we introduce the prismatic  $\langle a \rangle$  type loop in grain 1 by displacing all the atoms according to the anisotropic displacement field of the dislocation loop [55, 56]. We study the interaction of this prismatic  $\langle a \rangle$  type loop with the grain boundary and analyze the defects generated in the adjacent grain due to this interaction.

# 3.4 Results

Figure 3.6 shows the interaction of  $\langle a \rangle$ -type loop on the prismatic plane in grain 1 and the grain boundary. To study the interaction behavior, we apply incremental values of resolved shear strain on the dislocation loop plane, i.e., prismatic plane, and find the minimum required strain component at which the loop starts to move. At the critical resolved shear strain of  $\gamma_{RSS} = 0.0355$  on the prismatic plane, dislocation loop starts to move.

Figure 3.6 (b)-(d) show the snapshots of the simulation cell after 400, 1600, and 2400 relaxation steps. As the loop expands and reaches the boundary, it begins to interact with the boundary and generates additional defects in the adjacent grain.



**Figure 3.6:** Interaction of imposed prismatic loop in the lower grain and the random grain boundary. Snapshots of simulations depicted after (a) 0, (b) 400, (c) 1600 and (d) 2400 relaxation steps under the applied strain with the resolved shear strain component of  $\gamma_{RSS} = 0.0355$  on the prismatic loop plane. Non-hcp atoms are only shown to avoid confusion. Green ribbon shows the thickness of 20 Å where atoms are fixed in positions.

Common neighbor analysis (CNA)[70] of the generated defects is depicted in Figure 3.7. To find the crystallographic morphology of defects, we reorient the cell such that the pyramidal-II plane normal is aligned along *Z*. Figure 3.7 (b),(c) show the configuration of slipped and the hcp bulk atoms, respectively. Our measurements indicates that the misorientation between slipped and non-slipped hcp atoms matches the angle between two pyramidal slip plane normals  $(34.26^{\circ})$  suggesting that the atoms tend to slip on the pyramidal-I planes.



**Figure 3.7:** Analysis of the generated defect in grain 2 as a result of  $\langle a \rangle$ -type prismatic loop and GB interaction. (a) shows the generated defect reoriented such that X and Z are along  $\frac{1}{3}[2\overline{1}\overline{1}3]$  and  $(\overline{2}112)$  directions, respectively. (b) shows the slip of atoms on the {1011} pyramidal-I plane within the parent hcp lattice orientation where { $\overline{2}112$ } pyramidal-II planes lie on XY plane presented in (c).

After 2400 relaxation steps, incoming  $\langle a \rangle$ -type dislocation dissociates into the partial dislocations. The trailing partial is located at the boundary, making it difficult to identify the character of residual component on the boundary. However, the leading component is of  $\frac{1}{3}\langle 1\bar{1}00 \rangle$  Shockley partial character, which is glissile on the basal plane and leaves behind behind a locally fcc stacking fault. CNA analysis on the G2, as shown in Figure 3.8, elucidates that the lattice reorientation occurs in the middle of the grain separated from matrix by the interface colored in purple. Inspection of atomic structure in G2 shows that prismatic and basal planes meet at this 3D interface face-to-face. This type facet is known as basal-to-prismatic (BP) interface and has been observed in both experiments and simulations before [61, 71, 72, 73, 74, 75, 76, 77] and observed during the formation and growth of {1012} twins in hcp materials. We also find that the dissociated partials on the basal planes tend to cross-slip on the next basal planes. This leads to the further dissociation and cross-slip process.

Next, we perform dislocation analysis on the generated defects to characterize the dislocations responsible for the observed slip. Figure 3.10(a)-(b) show the character of nucleated dislocations from the grain boundary using dislocation extraction algorithm (DXA) within OVITO [78, 79]. Proportional lengths of the full and partial dislocations in the bicrystal are shown in Figure 3.9. The nucleated partials are mainly of  $\frac{1}{3}\langle 1\bar{1}00\rangle$ ,  $\frac{1}{9}\langle 1\bar{1}03\rangle$  and  $\frac{1}{9}\langle 2\bar{2}0\bar{3}\rangle$ characters. It is also important to note that these partials mainly have the edge and mixed character while some screw components are also observed. Previous studies on other hcp systems showed that it is energetically favorable for  $\langle c + a \rangle$ -type dislocations to dissociate into the partials with the same Burgers vector characters as of those identified and reported in the present work [80, 81, 82, 83]. More in depth analysis such as generalized stacking fault energy calculations not only along the exact  $\langle c + a \rangle$  but also along slightly off path using DFT is required to identify the energetically favorable dissociation paths in  $\alpha$ -Ti. This part of the project is currently an ongoing work.



**Figure 3.8:** Local crystallographic orientation analysis of the generated defect in grain 1 using common neighbor analysis. (a) depicts the generated defect within hcp atoms colored in purple and the hcp atoms colored in red which are removed in (c) to only show the defect. (b) and (c) enlarges the enclosed region which shows multiple partial dislocations cross-slip, leaving behind basal stacking fault regions colored in green. Misorientation analysis shows that hcp atoms are reoriented within the grain and the defect colored in purple acts as a basal-to-prismatic interface.



**Figure 3.9:** Analyzing the dislocation characters within the bicrystal. Generated dislocations in the grain 2 are mainly characterized as  $\frac{1}{9}\langle 2\bar{2}0\bar{3}\rangle$ ,  $\frac{1}{3}\langle 1\bar{1}00\rangle$  basal Shockley partial and  $\frac{1}{9}\langle 1\bar{1}03\rangle$ . Other type of partial dislocations are identified which embrace less than 9% of total dislocations length and categorized as *other*.

Figure 3.10 (c)-(d) enlarges the side view of dislocation analyses within the nucleated embryo. Several occurrences of dislocation cross-slips on the basal planes are observed. These cross-slips happen at the points where dislocations dissociate and become immobile on their glide plane. Similar observation is previously identified in experiments as discussed below.

Farenc *et al.* studied the mechanism of prismatic glide in  $\alpha$ -Ti at low temperatures using *in situ* experiments [84]. They found that the deformation in the prismatic plane of high purity Ti is controlled by the jerky movement of rectilinear dislocations. This observation is in agreement with the previous *in situ* observations where the glide is controlled by frictional forces resulting from the dissociation or spreading of the screw dislocations out of their glide plane [85, 86]. Farenc *et al.* also observed extensive cross-slips on the basal and first order pyramidal planes in high purity Ti samples. They explained that the locking-unlocking mechanism governs the deformation where the dislocation motion can take alternatively two states of different energies. The locking state where the dislocation



**Figure 3.10:** Dislocation analysis of the generated defect around the stacking fault. (a,d) and (b,c) represent the dislocation Burgers vector character and type (screw,edge), respectively. Nucleated dislocations dissociate into partials leaving behind stacking faults (colored in green) on the basal planes.

is immobile in the dynamic sequence and unlocking process which is done through the cross-slip. The glissile configuration corresponds to the planar dislocation dissociation on the prismatic and pyramidal planes when the stress orientation is favorable.

Our findings show the similar mechanism as observed in the experimental work by Farenc *et al.* Similar to [84], we also identify the jerky motion of partial dislocations dissociated on basal, prism and pyramidal-I planes. Our simulations show that there are multiple occurrences of dislocation dissociation which can act as the sessile locking point. Consistent with the experimental results, we also observe that the unlocking process is a done through a cross-slip as illustrated in the Figure 3.10.

#### 3.5 Concluding Remarks

In this chapter, we studied the role of strain transfer on the activation of deformation twinning at grain boundaries in  $\alpha$ -Ti. While slip-stimulated twinning was more likely displayed in hard/soft grain pairs with a large Schmid factor for twinning and a high m', some outlier cases were observed where slip in a soft oriented grain did not nucleate twin in the adjacent hard grain. We model one of these outlier grain pairs using atomistic simulations. We find that  $\langle a \rangle$ -type prismatic slip in soft grain did not nucleate twinning in the adjacent grain, in consistent with experimental observations. Moreover, further strain transfer led to the nucleation of additional defects; this interaction created a 3D basal-toprism facet in the middle of the hard grain and multiple cross-slips within the reoriented region inside the embryo. Dislocation analysis of these generated defects show that the cross-slip occurs at the locking points where partial dislocations intersect; a mechanism that has been observed in previous experimental works [84, 87]. Presence of the BP facets has been extensively observed during the nucleation and growth of  $(10\overline{1}2)$  twins in hcp systems [61, 71, 72, 73, 74, 75, 76, 77]. This can potentially be a precursor for the nucleation of 3D twins. Nucleation of favorably oriented twins can be triggered by the change in the local stress state close to the grain boundary due to the localized prismatic slip. Therefore, we can expect that higher local stress is necessary in addition to a high Schmid factor and m' parameter for slip-stimulated nucleation of the twin.

# Chapter 4: First-principles prediction of oxygen diffusivity near the $(10\overline{1}2)$ twin boundary in titanium

The work described in this chapter is a modified version of the following reference that has been published by M.S. Hooshmand *et al.* M.H. performed all the DFT and diffusion calculations. C.N. assisted in DFT cell size check and site energy calculations. Project is designed by M.G. and supervised by M.G. and D.T. Manuscript was written by M.H. and revised by M.G.

• **M.S. Hooshmand**, C. Niu, D.R. Trinkle, M. Ghazisaeidi, "First-principles prediction of oxygen diffusivity near the (1012) twin boundary in Titanium", *Acta Materialia (2018)* (link)

In this chapter, diffusivity of oxygen interstitials around a (1012) twin boundary in titanium is studied. First, all possible stable interstitial sites around the twin boundary are identified. Using density functional theory, the corresponding site energies and transition energy barriers for jumps between these sites are computed. Site energies and the barriers are consistently lower than in bulk, suggesting the higher tendency of oxygen to segregate to the twin boundary region. Using the site and transition energies and an exact solution to the master equation, diffusivity of oxygen in presence of the twin boundary is computed. Results show that the diffusivity around the boundary is enhanced in all directions. Enhanced diffusivity towards the boundary determines the feasibility of oxygen segregation to favorable sites at the boundary, while increased diffusivity in the boundary plane provides a path for fast diffusion of oxygen. This result reveals the underlying mechanism governing the slow growth of  $(10\overline{1}2)$  twin by pinning at the segregated oxygen interstitials.

#### 4.1 Introduction

One of the methods to improve or control the mechanical properties of materials is by alloying and chemistry change. Oxygen, as a common alloying element, is found to increase the tensile and fatigue strength of Ti by hindering the dislocation motion at the cost of decreasing the ductility and fracture toughness [5, 17]. Although twinning is frequently observed in commercially pure  $\alpha$ -Ti, it has not been reported previously in Ti alloys with significant amounts of  $\alpha$ -stabilizing solutes such as substitutional Al and interstitial oxygen. Twinning in Ti is believed to be suppressed by such elements [88], however, the underlying mechanism is unidentified. Atomistic simulations would help to obtain a better understanding of thermodynamics and kinetics of oxygen near Ti twin boundaries.

The first density functional theory (DFT) study, by Ghazisaeidi and Trinkle, has shown that oxygen prefers octahedral interstitial sites at (1012) TB [89]. In another DFT study, Liang and Hardouin Duprac showed that oxygen enhances the stiffness of  $\alpha$ -Ti as well as the stability of {1012} and {1122} TBs while decreasing the stability of {1011} and {1121} boundaries [90]. Moreover, Wu and Trinkle proposed a multi-state diffusion (MSD) based model to quantify the oxygen diffusion in the bulk Ti [1]. They concluded that the diffusion of oxygen is nearly isotropic along  $\vec{c}$  and basal planes. Scotti and Mottura also investigated the migration mechanisms of oxygen in bulk  $\alpha$ -Ti using DFT and kinetic Monte Carlo (KMC) simulations to find the diffusion coefficients [91]. Finally, Joost *et al.* combined DFT and classical potential calculations using a modified embedded atom method (MEAM) potential, with some reported discrepancy between DFT and MEAM predictions [92]. They then proceeded to calculate the transition energy barriers with MEAM only and overall, found lower energy barriers for oxygen jumps between various interstitial sites near the boundary. However, their study ends with reporting individual site and barrier energies and does not provide the collective diffusivity of oxygen within the interface.

Here, we compute all site and transition energy barriers with DFT. We then use an exact solution to the diffusion master equation [93] to obtain the oxygen diffusivity near ( $10\overline{1}2$ ) TB and conclude that diffusivity is enhanced near the boundary. In addition to predicting the diffusivity, our analysis improves upon site and transition energy calculations presented in [92] as follows. First, previous work by Ghazisaeidi and Trinkle [89] shows the importance of sufficient simulation sizes to avoid spurious interaction of oxygen with its periodic images. Therefore, all of our calculations are performed with supercells with a thickness of 3a along [ $1\overline{2}10$ ] direction where a is the Ti lattice constant. We find this increased simulation size to be essential, since supercells of smaller size, such as the 2a thick cell used in [92] cannot capture all stable interstitial sites near the twin boundary; oxygen, placed immediately above the boundary, pushes the boundary one layer further away after full relaxation. This does not happen with a larger supercell, where errors caused by periodic boundary conditions are minimized. Second, in spite of occasionally significant– up to 300 meV for the sites near the twin boundary– site energy differences between DFT and MEAM, all energy barriers in [92] are computed with MEAM.

Despite great interest on impurity diffusion around the boundaries, a quantitative and conclusive study of oxygen segregation to the twin boundary does not yet exist [19, 20,

21, 92]. In addition, due to the difficulties involved in measuring the accurate basic diffusion data experimentally, predicting the transport rates using first-principle data and the exact diffusion model is of high interest. Accurate determination of the diffusion mechanisms around interfaces requires more detailed atomic-scale analysis to identify the diffusion paths and quantify the anisotropic diffusivity around the boundary.

The aim of this chapter is to show the mechanism and kinetic feasibility of oxygen to migrate and then segregate to the twin boundary using first-principles. Section 4.2 contains the computational details. Calculations of the stable structure of  $(10\overline{1}2)$  TB and the relative formation energy of oxygen interstitials in and around the TB are presented in Section 4.3. Section 4.4 presents the computation of the transition energy barriers for various possible networks of jumps between interstitial sites. Finally, we use these values in Section 4.5 to calculate the diffusivity of oxygen in the vicinity of the TB and conclude in Section 4.6.

#### 4.2 Computational Method

First-principles calculations are performed with VASP [94, 95], a plane wave based density functional theory code, using projector augmented wave (PAW) method within the generalized gradient approximation (GGA)[32]. We use Methfessel-Paxton smearing of 0.15 eV and a plane wave cut-off of 500 eV. A double twin boundary geometry, with 10 atomic layers between the twin boundaries, is considered to maintain the periodicity along all three directions. With the above setting, a *k*-points mesh of  $3 \times 4 \times 1$  leads to  $\approx 0.1 \text{ meV}/\text{atom error}$  in the accuracy of site energies. A specific site energy is defined as the difference between the energy of the supercell with oxygen at the corresponding interstitial site and that of a "bulk-like" octahedral site at maximum distance from both twin boundaries. Site energy calculations are converged until the the forces are smaller

than 10 meV/ Å. Figure 4.1 shows the  $(10\overline{1}2)$  twin geometry supercell used for the site energy and transition barrier calculations. Note that in order to approximate the dilute limit, the supercell has a thickness of 3a; a = 2.9235 Å in  $[1\overline{2}10]$  direction, to minimize the interaction between oxygen and its periodic images [89]. This larger thickness is crucial, particularly since some of the twin boundary interstitial sites are not stable with a supercell thickness 2a; during relaxation of the atomic positions, the relative position of oxygen and TB changes, altering the interstitial site type.

We use transition state theory to calculate the energy barrier between various interstitial sites. Climbing-Image Nudged Elastic Band (CI-NEB) method [96, 97] is used with constant cell size, one intermediate image and a force criterion of 20 meV/Å. Attempt frequency for each transition v, is derived using the Vineyard's equation [98] as:

$$\nu = \frac{\prod_{i=1}^{3N} \nu_i}{\prod_{i=1}^{3N-1} \nu'_i}$$
(4.1)

in which  $v_i$  and  $v'_i$  are the stable normal mode frequencies at the local energy minimum and saddle point configurations, respectively. Only considering the oxygen attempt frequencies and neglecting the softening of the nearest Ti atoms is shown to underestimate the prefactors by less than 25% [1]. To obtain these quantities using VASP, finite difference small displacement method is implemented, in which each ion is displaced in the direction of each Cartesian coordinate. Then, the Hessian matrix is computed from the resulting forces. Individual phonon frequencies are the square root of the eigenvalues of the Hessian matrix [99, 100].



**Figure 4.1:** Twin geometry supercell. (a)  $X([\bar{1}011])$  and  $Y([1\bar{2}10])$  directions are twice and three times the single periodicity of the twin geometry unit cell, respectively. This supercell is used for all of the site energy and transition barrier calculations. The stable octahedral, crowdion, hexahedral and tetrahedral sites for oxygen are indicated by O (red), C (green), H (light brown) and T(grey), respectively. Dotted red line encloses the cell used for the diffusion coefficient calculation in the Section 4.5. (b) The inset shows a magnified view of the positions of all the nonequivalent stable sites within the supercell. All other sites can be obtained from these positions by symmetry and are considered in constructing the transition network and diffusion calculations. The crowdion sites, indicated in the parentheses, are located at different depths along the Y direction compared to the nearby octahedral sites. L1-L4 label the atomic layers from the closest layer to the TB to the bulk-like region away from the boundary. The star shows the bulk-like reference octahedral site used for the site energy calculations. Oxygen at H2 hexahedral site relaxes to the nearby tetrahedral. The black triangle shows the unstable crowdion site near the twin boundary. The distortion of host atoms due to the relaxations is not shown here to avoid confusion.

#### 4.3 Site Energies

Figure 4.1 shows the position of all stable oxygen interstitial sites in the twin geometry. Octahedral, crowdion, hexahedral and tetrahedral sites are indicated by O, C, H and T, respectively. The stable sites enclosed in the box are repeated through the entire supercell and considered in the transition network. L1-L4 label the layers of atoms with varying distance from the TB, with L1 being the closest layer and L4 the bulk-like region, farthest from the boundary. We find that the presence of (1012) TB affects the stability and site energy of different interstitial sites. For instance unlike in bulk Ti, tetrahedral sites are stable in the vicinity of the twin boundary. Figure 4.2 shows the relative site energies  $\Delta E_i$ , defined as the difference between the energy of the supercell with oxygen at the corresponding site and that of a supercell with oxygen at the reference octahedral site. These site energies are listed in the Table 4.1.



**Figure 4.2:** Relative site energy of the stable interstitial sites in the twin geometry, where zero energy corresponds the bulk octahedral site. Energies for octahedral, crowdion, hexahedral and tetrahedral sites are shown with respect to the distance from  $(10\overline{12})$  twin boundary. Dashed lines show the division of the cell to different layers from L1 closest layer to and L4 the farthest layer from the TB.

To investigate all possible stable interstitial sites on the twin boundary, we calculate the potential energy surface (PES) of oxygen on the boundary. An example of the application

of this method is presented in [101]. The PES is determined by sampling 77 points within the smallest periodic unit of twin boundary plane. For each sample point, a separate DFT calculation is performed, allowing for the local relaxation of neighboring Ti atoms on the boundary and fixing the oxygen and other Ti atoms until the force criterion described in Section 4.2 is achieved. Interpolating between the energies gives the PES shown in Figure 4.3. This analysis indicates that, even for the distorted twin interface, all possible stable interstitial sites are among the high symmetry interstitial positions. In case of hcp lattice, the high symmetry interstitial sites are the locally deep minimum octahedral and the shallow minimum at tetrahedral and crowdion sites on the boundary. As the site distance from TB increases, the bulk structure is restored and the site energies approach those in bulk Ti. The most significant change in site energies occurs in L1 where the twin octahedral sites have lower energies than the reference site and the stable tetrahedral sites have comparable energies to hexahedral sites in bulk.

Joost *et al.* have previously shown that the crowdion site indicated by black triangle in Figure 4.1 as well as the hexahedral H2 are stable sites for oxygen [92]. However, we find that oxygen at this crowdion site and H2 relax to the nearby tetrahedral sites. Our calculations show that the crowdion sites located behind O3, O4, O5, O6, O7 and O8 are unstable whereas C0, C0', C1, C2, C3 and C4 sites in L1 and L2 layers are stable. Finite-difference small displacement phonon analysis through DFT [102, 103] on these high energy crowdion sites shows no imaginary frequency mode for the oxygen atom in any of the three reciprocal lattice directions confirming that these sites are stable for oxygen at 0 K. These new stable sites near the TB linked with the other stable sites generate a connected network of paths for oxygen diffusion in the twin geometry.

Site	d(A)	Energy (eV)	Site	d(A)	Energy (eV)	Site	d(A)	Energy (eV)
Octahedral			Crowdion			Hexahedral		
01	0	-0.082	<b>C</b> 0	0	1.234	H1	2.02	0.920
O2	0	-0.096	C0′	0	1.159	H3	4.28	1.232
O3	2.52	0.145	C1	1.26	1.939	H4	4.03	1.133
O4	2.52	0.054	C2	3.02	1.790	H5	6.05	1.113
O5	4.03	-0.050	C3	5.04	1.566	H6	5.80	1.008
O6	4.03	-0.071	C4	5.04	1.386	H7	7.56	1.143
<b>O</b> 7	5.54	-0.014	C5	6.55	1.700	H8	7.81	1.163
<b>O</b> 8	5.54	-0.009	C6	6.55	1.580	H9	9.32	1.101
O9	7.56	-0.047	C7	8.06	1.631	H10	9.83	1.098
O10	7.56	-0.017	C8	8.06	1.551	Tetrahedral		
O11	9.32	-0.029	C9	7.56	1.533	T1	0	1.095
O12	9.32	0	C10	7.56	1.676	T2	0	1.327
			C11	9.32	1.638	H2	2.52	1.025
			C12	9.32	1.686			

**Table 4.1:** Site energies for oxygen at different stable interstitial sites. The relative formation energy (eV) and the distance from the boundary  $d(\text{\AA})$  for each site is listed (cf. Figure 4.1).



**Figure 4.3:** Potential energy surface (PES) of oxygen along  $\{10\overline{1}2\}$  twin boundary. Incorporating the symmetry of the cell, PES calculations are performed on the smallest periodic unit of the twin boundary plane, depicted in the left figure. Relative formation energies for oxygen are given in eV.

### 4.4 Energy Barriers for Diffusion

Next we calculate  $E_{ij}$ , the energy barrier for the transition between interstitial sites *i* and *j*, using the climbing-image nudged elastic band CI-NEB method with one intermediate image for most cases [96, 97]. Due to the distortion near the TB, for some of the paths such as octahedral to tetrahedral jumps, three intermediate images are necessary to meet the NEB convergence criterion. Figure 4.4 shows the energy barriers for the octahedral to octahedral (o-o), octahedral to tetrahedral (o-t), octahedral to hexahedral (o-h), octahedral to crowdion (o-c), tetrahedral to crowdion (t-c) and hexahedral to crowdion (h-c) jumps at different distances from the TB. Dashed lines show the bulk value of each type. Energy barriers in L4, the farthest layer from (1012) TBs, converge to bulk values, which also match well with the previously reported values [1]. However, the energy barriers decrease significantly around the TB in L1. The twin boundary reduces the o-o jump barriers from

3.2 eV in bulk to 2.3 eV. This highlights a major difference between the diffusion jump network in bulk versus the boundary region; unlike the high-barrier o-o jumps in bulk, in the twin boundary region, direct o-o transition barriers are comparable to those of o-h jumps. A similar trend is observed for the o-h jumps where the energy barrier decreases from 2.2 eV in bulk to 1.5 eV near the boundary.

Additional features emerge for the crowdion sites as follows. Near the twin boundary, our calculations show that the energy barrier associated with jumps out of C1-C4 are in order of  $\sim 0.03 - 0.08$  eV, much smaller than barriers for jumps to these sites, which are around 2 eV. Therefore, given the sufficient thermal energy, oxygen atoms at these metastable crowdion sites overcome this shallow barrier and jump back to the nearby octahedral or hexahedral sites. This suggests that these crowdion sites will not be able to achieve thermal equilibrium, even at moderate to low temperatures. On the other hand, we find that for the o-o and o-h jumps involving these crowdion sites in their minimum energy path, the saddle point energies are close within  $\sim 10\%$  of the nearby high energy metastable crowdion, suggesting that these sites can possibly act as the transition states at higher temperatures. Thus, while we remove C1-C4 sites as possible metastable sites from the diffusion network, the nearby saddle points will still contribute to the diffusion network as transition states. All other crowdion sites are considered as metastable sites in the diffusion path.

Attempt frequencies for various jumps around the TB compared with the same type of jumps in the bulk-like environment are listed in Table 4.2. We find about 13%-20% increase in the prefactors of o-o and o-h jumps near twin boundary compared to the bulk-like region. This is accompanied by the hardening of the rotational frequency modes for oxygen at the octahedral and hexahedral sites near the boundary. Besides the more significant impact of

reduction in migration barriers for the jumps near the twin boundary, the increase in attempt frequencies can also contribute to the higher diffusion.

In addition, new tetrahedral sites in the boundary region create more pathways for diffusion of oxygen. It is expected that a larger network of jumps, along with the reduction in the transition energy barriers around the twin, increase the mobility of oxygen interstitials in the vicinity of the TB compared to bulk. Next, we quantify the diffusivity of oxygen near the twin boundary with input from the DFT-calculated site energies and transition barriers.

**Table 4.2:** Attempt frequencies for different transition networks. The bulk values of the attempt frequencies correspond to the jumps in L4 layer, which represents the bulk-like environment compared with the same type of jumps in the vicinity of  $(10\overline{1}2)$  TB (cf. Figure 4.1). The jump vector of each transition is indicated in the second column. *z* is the Wyckoff coordinate of the tetrahedral sites along the  $\vec{c}$  axis in a typical hcp lattice.

		v[THz]	
Site	Direction	Bulk	Twin(L1)
		(L4)	
$o \rightarrow o$	$\langle 000\frac{1}{2} \rangle$	13.59	16.29
$o \rightarrow h$	$\langle \frac{1}{3} \frac{\overline{1}}{3} 0 \overline{\frac{1}{4}} \rangle$	12.51	14.14
$h \rightarrow o$	$\langle \frac{1}{3} \frac{1}{3} 0 \frac{1}{4} \rangle$	10.52	12.08
$o \rightarrow t$	$\langle \frac{1}{3} \frac{1}{3} 0z \rangle$	-	11.82
$t \rightarrow o$	$\langle \frac{1}{3} \frac{1}{3} 0 z \rangle$	-	8.77
$c \rightarrow t$	$\langle \frac{1}{6} \frac{1}{6} \frac{1}{3} \overline{z} \rangle$	-	6.89
$t \rightarrow c$	$\left\langle \frac{1}{6} \frac{1}{6} \frac{1}{3} \overline{z} \right\rangle$	-	14.72
$h \rightarrow c$	$\langle \frac{1}{6}0\frac{1}{6}\frac{1}{4}\rangle$	5.80	9.06
$c \rightarrow h$	$\langle \frac{1}{6}0\frac{1}{6}\frac{1}{4}\rangle$	13.65	1.45
$o \rightarrow c$	$\langle \frac{1}{6} \frac{1}{6} \frac{1}{3} \frac{1}{3} 0 \rangle$	21.17	24.70
$c \rightarrow o$	$\langle \frac{\ddot{1}}{6} \frac{\ddot{1}}{6} \frac{\ddot{1}}{3} 0 \rangle$	16.62	5.21

#### 4.5 Diffusion coefficient

In this section, we calculate the oxygen transport coefficient in a Ti crystal containing a twin boundary by finding steady-state solutions to the master equation [93]. For a simple



**Figure 4.4:** Transition energy barriers for (*a*) octahedral to octahedral and octahedral to tetrahedral, (*b*) octahedral to hexahedral, (*c*) octahedral to crowdion and tetrahedral to crowdion, and (*d*) hexahedral to crowdion jumps. The energy barriers are calculated between interstitial sites at various distances from the twin boundary from L1, closest layer to the boundary to L4 where bulk structure is retrieved. Dashed lines in each figure show the corresponding transition barrier in bulk. Note that tetrahedral sites are only stable in L1 and L2. Due to the shallow barrier of jumps from crowdion sites in L1 and L2 layers, C1-C4 are excluded as metastable sites from network. The L1 barriers indicated in (*c*) – (*d*) correspond to the jumps with crowdion sites located on the twin boundary as one of the metastable sites.

transition from site *i* to *j*, the absolute rate of a transition is defined as  $\rho_i \lambda_{ij}$ , where  $\rho_i$  and  $\lambda_{ij}$  are the probability of site occupancy and the transition rate from site *i* to *j*, respectively.  $\rho_i$  is proportional to  $\exp(-\Delta E_i/k_BT)$  and  $\lambda_{ij} = v_{ij}\exp(-E_{ij}/k_BT)$ , where  $\Delta E_i$  is the relative formation energy of each interstitial site calculated in 4.3,  $E_{ij}$  is the transition energy barrier reported in 4.4 and  $v_{ij}$  is attempt frequency prefactor listed in Table 4.2 for each jump. The general expression for the anisotropic diffusivity tensor from site and transition state energies is derived in [93] and is given by:

$$\underline{\mathbf{D}} = \frac{1}{2} \sum_{ij} \delta x_{ij} \otimes \delta x_{ij} \lambda_{ij} \rho_i + \sum_i b_i \otimes \gamma_i$$
(4.2)

where  $\delta x_{ij}$  is the displacement of the diffusing atom from site *i* to site *j*, *b<sub>i</sub>* is the scaled velocity vector corresponding to the bias jumps from site *i*, and  $\gamma_i$  is the bias-correction vector. The first and second terms in Equation 4.2 represent the contributions from uncorrelated and correlated jumps, respectively. The bias term is nonzero when there are unbalanced hops from site *i*. Taking advantage of the crystal symmetry simplifies the above expressions. We use an open-source implementation of the general solution [104]. In order to take into account the broken symmetry that the twin boundary introduces to the Ti crystal, we modify the crystallographic symmetry operations in the code and adjust it to the cell containing the TB. In addition, we generate the additional interpenetrated jump network between the stable sites on both sides of the boundary that are connected via a mirror symmetry operation.

To study the diffusion anisotropy in bulk  $\alpha$ -Ti using the master equation based model, we perform DFT calculation on the 4×4×3 (96 atoms) hcp supercell with 5×5×3 *k*-point mesh and the same numerical settings as explained in Section 4.2. Our bulk site energies and transition barriers match well with the previously reported values by Wu and Trinkle [1]. We obtain the relative formation energy of 1.64 eV for hexahedral sites with reference to the octahedral and the transition barrier energy of 3.30 eV and 2.03 eV for o-o and oh jumps compared to the reported hexahedral relative site energy of 1.19 eV and the o-o and o-h transition barriers of 3.25 eV and 2.04 eV, respectively. Figure 4.5 shows the bulk diffusivity evaluated using the analytical master equation based diffusion model compared to the MSD model and other experimental values reported in the literature [1, 10, 11]. We conclude that similar to the MSD formalism, master equation based diffusion model also predicts the isotropic diffusion of oxygen in bulk  $\alpha$ -Ti.



**Figure 4.5:** Isotropic diffusion in bulk hcp  $\alpha$ -Ti. We compare the diffusivity evaluated using the master equation based diffusion model implemented in the current study with the previously reported multi-state diffusion model in hcp bulk  $\alpha$ -Ti [1]. Very close values of the diffusivity in both basal plane and along the  $\vec{c}$  axis of hcp cell suggests the nearly isotropic diffusion in bulk hcp  $\alpha$ -Ti. *Y* axis in the figure is in logarithmic scale. The experimental data from the literature is also depicted for the sake comparison[10, 11].

Then, we test our predictions by comparing the diffusivity in the bulk-like L4 region with previously published literature. Figure 4.6 shows that the bulk diffusivity predicted here agrees well with that calculated by Wu and Trinkle using first principles calculations and a MSD formalism [1] and experimental values[10, 11].



**Figure 4.6:** Diffusivity in bulk hcp  $\alpha$ -Ti compared to a previous DFT calculation [1] and experimental predictions[10, 11]. Our diffusivity values are in good agreement with the reported Multi-state-Diffusion-based diffusivity by Wu and Trinkle [1].

Next, we calculate the diffusivity of oxygen near the TB. Correlated random walk is the source of complexity in diffusion calculations and depends on the crystal symmetry of the structure [105]. It is previously shown that among different interstitial sites, only tetrahedral sites can contribute to the correlated diffusion in bulk  $\alpha$ - Ti [93]. However, oxygen is unstable at the tetrahedral interstitial site in the bulk  $\alpha$ - Ti and this results in uncorrelated diffusion. Newly found stable tetrahedral sites and the formation of new diffusion paths near the TB adds more complexity to the diffusion calculation near the twin boundary. In addition, the broken symmetry of the hcp lattice near the twin boundary leads to a nonzero bias term in Equation 4.2. The nonzero bias term requires careful consideration and is included in our diffusivity calculations. Figure 4.7 shows the diffusivity along directions in and perpendicular to the boundary. The diffusion coefficients are evaluated in the double twin boundary geometry "unit cell" with a single periodicity along X (6.86 Å) and Y(2.92 Å) directions, enclosed by red dotted line in the Figure 4.1. All symmetrically unique jumps have been taken into the account in the diffusion calculations by employing the periodic boundary conditions. The isotropic bulk diffusivity is also included for comparison. As shown in the figure, diffusivity is higher near the boundary, in all three directions, compared to bulk.

Furthermore, it is important to note that the small energy barrier of octahedral to tetrahedral jumps near the TB significantly contributes to the enhanced diffusivity in the vicinity of the TB. Figure 4.8 shows the contribution of tetrahedral sites to the diffusion coefficients. The results show that inclusion of tetrahedral sites in the diffusion network gives higher diffusivity, particularly in the direction perpendicular to the boundary. However, even without the tetrahedral sites, the twin boundary diffusivities are generally higher compared to bulk. This is expected, given the lower transition barriers for o-o and o-h jumps near the boundary.

In addition, the calculated diffusion coefficients are fitted to an Arrhenius model,  $D = D_0 \exp(-E_{act}/k_BT)$ , where D,  $D_0$ ,  $E_{act}$  and  $k_B$  are diffusivity, diffusion prefactor, activation energy barrier and Boltzmann constant, respectively. Table 4.3 compares the bulk and twin boundary  $D_0$  and  $E_{act}$  with published literature. The activation energy barrier is lower in the twin boundary region than in bulk in all directions. The lower energy barrier reported here is indicative of the feasibility and higher tendency of oxygen atoms to transport toward the boundary rather than remaining in the bulk-like region. Indeed, both energy and kinetic

analysis are crucial to investigate any segregation process. Enhanced diffusivity towards the boundary suggests the possibility of oxygen segregation to favorable sites at the boundary, while increased diffusivity in the boundary plane provides a path for fast diffusion of oxygen.



**Figure 4.7:** Diffusion coefficient in the presence of TB. Diffusivity along three lattice directions in the twin geometry is compared with the bulk diffusivity in a logarithmic scale. It is shown that the diffusivity increases near the TB. The green and black dashed lines show the Arrhenius fit to the diffusion coefficient data along the direction in and perpendicular to the TB, respectively.

### 4.6 Conclusion

We study the effect of (1012) TB on the diffusion of oxygen interstitials in  $\alpha$ -Ti, using DFT, and show that the formation energy of oxygen at octahedral and hexahedral sites are



**Figure 4.8:** Contribution of tetrahedral interstitial sites in the oxygen diffusion near the TB. (a) filled symbols show the diffusion coefficients evaluated by considering the tetrahedral sites in the network (the same data as depicted in Figure 4.7) compared to the diffusivity without considering the tetrahedral sites in the network. Bulk diffusion is also included for comparison. (b) the ratio of computed diffusivity using the network with tetrahedral sites to the network without tetrahedral sites. This shows including the tetrahedral sites in the diffusion network has a more highlighted impact on the diffusivity toward the TB compared to other two directions.

**Table 4.3:** Arrhenius fit to the diffusivity data derived from the diffusion model based on the solution to the master equation. Diffusivities are fit to the  $D = D_0 \exp(-E_{act}/K_BT)$  equation over the temperature range of 600 – 1100 K, where D,  $D_0$  and  $E_{act}$  are diffusivity, diffusion prefactor and activation energy barrier, respectively. These values are compared to our bulk-like region calculation as well as previous analytical model [1]. These results show the decrease in the overall activation energy of jumps near the TB, therefore, higher rate of diffusion.

Geometry	$D_0(m^2/s)$	$E_{act}(eV)$
Wu et al. [1]	$2.18 \times 10^{-6}$	-2.08
Bulk	$7.35 \times 10^{-7}$	-1.97
Twin(x)	$2.58 \times 10^{-7}$	-1.51
Twin(y)	$1.70 \times 10^{-7}$	-1.33
Twin(z)	$1.35 \times 10^{-7}$	-1.31

lower near the TB than in bulk. In addition, we find three new stable tetrahedral sites, one at the distance of ~ 2.3 Å from the boundary and two on the TB. The energy barriers for transition between the twin boundary interstitial sites are also consistently lower than that in bulk. Using the site and transition energies and an exact solution to the master equation, we then compute the diffusivity of oxygen in the presence of the TB. The diffusivity in the "bulk-like" region agrees well with previous reports of the bulk diffusivity. Moreover, we conclude that the oxygen diffusion rate increases in the presence of  $(10\bar{1}2)$  TB in all directions, toward and parallel to the boundary plane. This suggests that  $(10\bar{1}2)$  TB can act as a two-dimensional sink for oxygen atoms, but the higher diffusivity along  $[1\bar{2}10]$ direction provides a fast migration channel along the TB. The increase in diffusivity of oxygen near the TB also shows that oxygen segregation to the twin boundary is kinetically feasible. This segregation could potentially result in pinning and therefore slower growth of  $(10\bar{1}2)$  TB, similar to what has been observed by substitutional solutes in [106]. Our analysis is applicable to other interstitials and boundaries and provides a tool for deriving more rigorous diffusivities to compare with experiments.

# Chapter 5: Quantitative analysis of uncertainty in self and solute diffusion calculations from first-principles

# The work described in this chapter is a modified version of the following preprint. M.H. performed the modeling and W.Z. did the experiments. Project is designed and supervised by M.G. and JC.Z. and W.W. The following preprint is written by M.H.

• W. Zhong, **M.S. Hooshmand**, M. Ghazisaeidi, W. Windl, JC. Zhao, "A comprehensive experimental and computational study of the diffusion and mobility of the Al-Mg binary system", (*under review*)

This chapter focuses on quantifying the uncertainty that arises from first-principles calculations in predicting diffusion coefficients. First, we identify different uncertainty sources. These sources include the diffusion model, energetic, entropic and attempt frequency calculations. Then, we quantify the variation in diffusion coefficients using different density functional theory settings and compare the results with experiments. This study demonstrates a framework to reliably predict the transport coefficients for any system of interest within the periodic table from atomistic simulations.

## 5.1 Introduction

Diffusion in materials plays an important role in understanding many fundamental properties such as corrosion, surface oxidation, recrystallization and precipitation. Developing new alloys requires extensive knowledge about the kinetics and mobility of different elements within a crystal. Magnesium (Mg) metal, one of the lightest structural materials, has a wide range of applications in the transportation sector. However, it suffers from a low ductility, which makes it difficult to form at room temperatures. Alloying is an effective method to further improve the damage tolerance of Mg. In particular, Aluminum (Al), Zinc (Zn) and rare earth (RE) solutes solutes can improve both strength and ductility of Mg. In-depth knowledge about the transport coefficients of solutes in the metals is required to understand the underlying mechanisms and to study the microstructure evolution.

Mg is commonly used in Al alloys while Al is the most widely used alloying element in Mg. Mg has hexagonal close packed (hcp) crystal structure while Al is stable in face centered cube (fcc) phase. Accurately determining the atomic mobility of Mg in Al and vice versa is essential for establishing reliable Al and Mg mobility databases. This requires having information about the transport coefficients of Mg/Al solutes in Al/Mg and vice versa at the metastable (hypothetical) phases, i.e. the hcp Al and fcc Mg phases. Due to the limitations in experimental measurements, computational models from first principles can be used to predict the diffusion coefficients in the metastable phases.

First principles calculations are invaluable tools to quantify diffusion coefficients, especially when there is not enough experimental data. However, there are some uncertainties involved in predicting accurate diffusion coefficients which need to be considered. Uncertainty in the results can stem from various sources. These sources include the diffusion model, energetic evaluation, vacancy concentration evaluation (in case of vacancymediated diffusion) and attempt frequency (prefactor) calculation. In this work, we study these uncertainty sources in Mg/Al self diffusion and inter diffusion calculations in stable hcp/fcc phases. The impact of each uncertainty source on the predicted diffusion coefficients is quantified from first principles calculations. Using the best settings for the stable cases, we then evaluate the diffusion coefficients in the metastable phases. Section 5.2 gives a brief overview about the various uncertainty sources. The computational method is explained in Section 5.3. Finally, the results and conclusions are discussed in Section 5.4 and Section 5.5.

#### 5.2 Uncertainty sources

One source of uncertainty in transport coefficient calculations is the diffusion model. One of the complexities involved in vacancy-mediated diffusion is the correlated random walk which is dependent on the crystal structure. This has been done by proposing specific solutions for different crystal structures, such as the five-frequency model for fcc [2, 107], and the eight- [108] and thirteen- [109] frequency models for hcp. One simplified constraint in all these methods is on the rates which do not arise from crystal symmetry. Also, the interactions are assumed to end beyond the first nearest-neighbor. Kinetic Monte Carlo [110, 111, 112, 113] is an alternative crystal-independent method, however it is not a practical method in cases where there are large differences in the vacancy-solute exchange rates. Recently, Dallas Trinkle developed an exact Green function approach to calculate the diffusion coefficients from first principles data avoiding uncontrolled approximations [105]. This method enables capturing the correlation factors based on the crystal structure of interest without making any simplified assumptions. Later, Agarwal and Trinkle found that the transitions in eight-frequency and thirteen-frequency models are incorrectly treated for hcp crystals [3]. The authors proposed a sixteen-frequency model that incorporates all uniquely independent transition paths for solute/vacancy transitions in hcp structures. We use this sixteen-frequency model for hcp and five-frequency model for fcc within the Green function based approach to evaluate the self and impurity diffusion in Mg/Al alloys and to quantify the uncertainty originating from the choice of diffusion model.

Uncertainty can also arise from the energetic evaluations in density functional theory (DFT) calculations. Site energies, energy barriers for solute/vacancy jumps, and vacancy formation energies (VFE) are the energetic components evaluated from first principles used as inputs to the diffusion models. The choice of pseudopotential and exchange-correlation (XC) results in different energetics and impacts the final diffusion coefficients by mainly contributing to the diffusion activation energy barrier. Here we quantify the difference in self and impurity diffusivities in Mg/Al pair using various functionals and show how this affects different components in diffusivity calculations.

Attempt frequency calculation also play an important role in evaluating the diffusion prefactor. Two well-known methods to evaluate attempt frequencies are finite difference small displacement method (FDM) [99, 100] and density-functional perturbation theory (DFPT) [114, 115]. In the current work, we also compare the attempt frequencies computed from each of these methods and quantify the difference it makes on the diffusion coefficients. It is also worth noting that the vacancy formation entropy is another important contributing factor in diffusion prefactor. Similar to VFE, the effect of different functionals on vacancy formation entropy and diffusivities are also investigated.

#### 5.3 Computational method

DFT calculations are performed using VASP package [95, 116, 117], a plane-waved based density functional code. We compare ultra-soft pseudopotential (USPP) [118] with projector augmented wave (PAW) [119, 120] formalism based potentials within the generalized gradient approximation (GGA) exchange correlation functionals. In particular, we implement Perdew-Burke-Ernzerhof [33] (labeled as PBE) and a modified version by incorporating surface energy error correction [121] (labeled as PBE-sol) functionals. A

plane-wave cutoff of 260 eV is used throughout the calculations. A  $4 \times 4 \times 3$  (96 atoms) and a  $3 \times 3 \times 3$  (108 atoms) supercell is employed for hcp and fcc structures, respectively. For electronic smearing, the first-order Methfessel-Paxton method [122, 123] with a smearing width of 0.2 eV is used. A  $6 \times 6 \times 6$  Monkhorst-Pack *k*-point mesh is used for Brillouin zone integration with a Monkhorst-Pack grid for all supercells.  $\Gamma$ -point is included in the *k*-mesh for hcp systems. Conjugate gradient method is used for minimizing the energy of all atoms until the forces are less than 0.1 meV/Å. The calculated lattice parameters using the settings above are a = 4.04 Å for fcc-Al, a = 4.51 Å for fcc-Mg, a = 3.69 Å;  $\frac{c}{a} = 1.41$  for hcp Mg and a = 3.29 Å;  $\frac{c}{a} = 1.44$  for hcp Al. Vacancy hop rate follows  $\omega = v_0 \exp(-E_a/k_BT)$ , where  $v_0$  is the attempt frequency and  $E_a$  the energy difference between saddle point and initial configuration, assuming transition state theory.  $k_B$  and T are Boltzmann constant and temperature, respectively.

To calculate the transition state configuration and energy, we use climbing-image nudged elastic band (CI-NEB) method with one intermediate image [97]. These CI-NEB calculations are continued until the forces are converged to within 5 meV/Å. Attempt frequency associated with each transition,  $\nu$ , in a supercell with N number of atoms is computed from Vineyard's equation:

$$v = \frac{\prod_{k=1}^{3N} v_k}{\prod_{k=1}^{3N-1} v'_k}$$
(5.1)

where  $v_k$  and  $v'_k$  are the real normal mode frequencies at the local energy minimum and saddle point configuration, respectively. We implement and compare FDM [99, 100] and DFPT [114, 115] approaches to calculate the restoring forces and derive the Hessian matrix. Individual phonon frequencies are the square root of the eigenvalues of the Hessian matrix. To evaluate the vacancy formation energy and entropy, we calculate the vibrational contribution to the free energy of both perfect and vacancy cells using the Phonopy package [124].

#### 5.4 Diffusion calculation

#### 5.4.1 Model

We calculate solute diffusion coefficients from the DFT inputs by following the Green function solution to the master equation approach [105]. Binding energy  $E_b$  between solutes (S) and vacancies (V) in a given crystal structure (with host atom A) can be calculated from:

$$E_b = E(A_{N-2}S_1V_1) + E(A_N) - E(A_{N-1}S_1) - E(A_{N-1}V_1)$$
(5.2)

where  $E(A_N)$ ,  $E(A_{N-1}S_1)$ ,  $E(A_{N-1}V_1)$  and  $E(A_{N-2}S_1V_1)$  are the energy of pure system with N atoms, a system containing a solute atom, a system containing a vacancy and a system containing a vacancy-solute pair, respectively.

For impurity diffusion calculation in fcc systems, we use five-frequency model [2, 107]. Figure 5.1 shows the five identical jumps representing the symmetrically unique vacancy/solute (solvent) jumps. These rates are defined as vacancy hops in the solvent  $(\omega_0)$ , vacancy rotation around the solute  $(\omega_1)$ , vacancy-solute exchange  $(\omega_2)$ , dissociation from  $(\omega_3)$  and association towards  $(\omega_4)$  the solute. Table 5.1 lists the attempt frequencies and migration barriers for the five frequencies for diffusion of Mg(Al) in fcc Al(Mg) along with the corresponding solute-vacancy binding energies.

To calculate the diffusion coefficients in hcp systems, we use sixteen-frequency model recently proposed by Agarwal and Trinkle [3]. Authors argue the previous standard eight-
[108] and thirteen- [109] frequency models treat the symmetrically inequivalent transitions as the same jump incorrectly and therefore proposed a corrected sixteen-frequency model. Figure 5.2 shows these symmetrically unique jumps in an hcp lattice following the notation in reference [3]. The symmetry-unique frequencies and solute/vacancy migration barriers are tabulated in Table 5.2 and Table 5.3.

For self-diffusion coefficients, the five-frequency model is reduced to one, vacancy jump to the nearest neighbor host atom. Similarly, sixteen-frequency jumps in hcp are reduced to two, vacancy jump to the nearest neighbor host atom on the basal and pyramidal planes. Table 5.4 lists the energy barriers and attempt frequencies for vacancy jumps in the elemental hcp and fcc systems.

Transition energies and attempt frequencies computed from DFT can be used to compute the Onsager matrix and the diffusion coefficient of solute impurities in the dilute limit [105]. Using this model, the solute-related diagonal term of the Onsager matrix,  $\underline{L}^{SS}$ , is calculated. In the dilute limit, the solute diffusivity tensor,  $\underline{D}^{S}$ , can be computed from the solute transport coefficient using the following equation:

$$\underline{\mathbf{D}}^{S} = k_{B}T\Omega(c^{s})^{-1}\underline{\mathbf{L}}^{SS}$$
(5.3)

where  $\Omega$  and  $c^s$  are volume per atom and vacancy concentration, respectively. In the global thermal equilibrium, vacancy concentration is:

$$c^{s} = \exp\left(-\frac{E_{\text{form}}^{V} - TS_{\text{form}}^{V}}{k_{B}T}\right)$$
(5.4)

where  $E_{\text{form}}^V$  and  $S_{\text{form}}^V$  are the vacancy formation energy and entropy, respectively. Note that  $E_{\text{form}}^V$  includes the zero-point energy. Vacancy formation energy and entropy are evaluated by calculating the Gibbs free energy of both the perfect supercell and the supercell with

a vacancy at elevated temperature within the quasi-harmonic approximation (QHA) from phonon calculations [125]. Calculated vacancy formation energies and entropies are shown in Table 5.5. Finally, diffusion coefficients *D* are calculated and fitted into the conventional Arrhenius form:

$$D = D_0 \exp\left(-\frac{Q}{k_B T}\right) \tag{5.5}$$



**Figure 5.1:** Five-frequency jumps in fcc crystal structure. Solute and vacancies are indicated by yellow sphere and white square, respectively. Blue spheres represent host atom.

# 5.4.2 Effects of exchange-correlation on diffusivities

First, we investigate the effect of different XCs on both transition barrier energies and vacancy formation energies and entropies. Figure 5.3 shows the calculated self-diffusion in fcc Al and hcp Mg using different XCs functionals of USPP and PBEsol compared with the experimental assessment done by Zhong *et al.* [12]. The choice of PBEsol for hcp Mg shows the best agreement with the experiments. We find that the PBEsol improves

rbesol). Auempuare calculated and o	irequencies irc compared. Soli	om both density runct ute-vacancy nearest-r	rional perturbation neighbor binding er	nergies are also	and nnite diffe listed.	srence memoa (	FDIM) using PAW-	r B E S OI T UN CH O N AI
System	Quantity	DFT Settings	Binding Energy (AV)	Solvent Diffusion	Rotation	Exchange	Dissociation	Association
		ocurres o	LINIES (UV)	$\omega_0$	$\omega_1$	$\omega_2$	$\omega_3$	$\omega_4$
Mg in fcc Al	$E^{mig}(eV)$	USPP	0.008	0.537	0.680	0.393	0.477	0.457
		PAW-PBEsol	-0.006	0.707	0.744	0.465	0.590	0.663
	$\nu(THz)$	DFPT	ı	6.475	9.309	43.783	10.264	6.064
		FDM	ı	14.814	3.152	4.832	8.842	18.128
Al in fcc Mg	$E^{mig}(eV)$	USPP	-0.01	0.361	0.284	0.541	0.410	0.407
		PAW-PBEsol	-0.038	0.378	0.317	0.611	0.365	0.444
	$\nu(THz)$	DFPT	ı	11.875	6.356	9.605	8.011	14.791
		FDM	I	16.879	33.407	57.861	338.230	20.771

**Table 5.1:** Migration barriers (eV) and attempt frequencies (THz) of jumps involved in the diffusion of Mg(Al) in fcc Al(Mg) within the five-frequency model [2]. Values calculated using ultra-soft pseudopotential (USPP) and the PBE functional are compared to the PAW with the PBEsol functional (PAW-DBEsol). Attempt frequencies from both density functional nerturbation theory (DFPT) and finite difference method (FDM) using PAW-PBEsol functional

	1b-6b	0.382	0.406	0.392	ı	0.410	0.414	8.566	3.660	0.381	0.528	2.952	3.257
_	1b- <u>4b</u>	0.383	0.408	0.399	ı	ı	ı	9.346	2.469	0.409	0.551	3.294	3.813
Dissociation	1b-4b	0.407	0.432	0.424	0.428	ı	ı	8.436	8.909	0.363	0.516	11.204	13.225
	1b-4p	0.407	0.431	0.426	ı	ı	ı	10.915	2.552	0.403	0.555	9.475	11.974
	1b-2p	0.458	0.481	0.472	ı	ı	ı	11.892	4.201	0.385	0.537	5.223	6.023
uo	1b-1p	0.303	0.326	0.318	0.310	0.320	0.343	8.686	4.043	0.541	0.696	25.784	32.697
eorientati	<u>1b-1b</u>	0.366	0.388	0.378	0.382	ı	0.372	7.628	10.442	0.452	0.597	14.070	13.131
R	1b-1b	0.225	0.251	0.240	ı	0.240	ı	7.313	4.419	0.621	0.768	6.471	9.229
Exchange	1b-sol	0.511	0.554	0.524	0.519	0.530	0.599	39.943	7.369	0.305	0.432	14.842	16.165
Binding Energy(eV)		-0.039	-0.046	-0.027	I	I	ı	I	I	-0.013	-0.069	I	ı
DFT Settings		USPP	PAW-PBEsol	Ref. [3]	Ref. [126]	Ref. [127]	Ref. [128]	DFPT	FDM	USPP	PAW-PBEsol	DFPT	FDM
Quantity		$E^{mig}(eV)$						$\nu$ (THz)		$E^{mig}(eV)$		$\nu$ (THz)	
System		Al in hcp Mg								Mg in hcp Al			

**Table 5.2:** Migration barriers (eV) and attempt frequencies (THz) for the diffusion of dilute Mg(Al) in hcp Al(Mg) from the 1b configuration following the notation in reference [3]. Migration barriers from previous DFT works are also included for comparison (cf. Figure 5.2 for notation and the caption in Table 5.1 for DFT settings interpretation).

	1p-5p	0.395	0.435	0.414	ı	ı	ı	187.88	12.181	0.420	0.590	19.901	19.747
Dissociation	1p-4p	0.391	0.418	0.409	0.414	0.410	0.418	10.072	4.663	0.399	0.546	7.847	6.032
	1p-3c	0.447	0.492	0.471	ı	ı	ı	9.341	4.271	0.376	0.523	8.438	8.665
	1p-2p	0.428	0.451	0.441	I	ı	I	13.030	3.706	0.370	0.522	3.820	3.525
ntation	1p-1b	0.295	0.319	0.311	0.306	0.310	0.326	9.771	2.818	0.545	0.702	16.976	21.210
Reorier	1p-1p	0.292	0.333	0.308	0.307	0.310	0.326	81.356	13.725	0.514	0.667	11.461	10.836
Exchange	1p-sol	0.546	0.595	0.567	0.560	0.570	0.654	52.310	7.388	0.294	0.423	19.994	19.316
Binding Energy(eV)		-0.031	-0.041	-0.020	I	ı	ı	ı	ı	-0.019	-0.074	ı	ı
DFT Settings		USPP	PAW-PBEsol	Ref. [3]	Ref. [126]	Ref. [127]	Ref. [128]	DFPT	FDM	USPP	<b>PAW-PBEsol</b>	DFPT	FDM
Quantity		$E^{mig}(eV)$						$\nu$ (THz)		$E^{mig}(eV)$		$\nu$ (THz)	
System		Al in hcp Mg								Mg in hcp Al			

**Table 5.3:** Migration barriers (eV) and attempt frequencies (THz) for the diffusion of dilute Mg(Al) in hcp Al(Mg) from the 1p configuration following the notation in reference [3]. Migration barriers from previous DFT works are also included for comparison (cf. Figure 5.2 for notation and the caption in Table 5.1 for DFT settings interpretation).

Quantity	DFT Settings	hcp Mg	fcc Al	fcc Mg	hcp Al
E <sup>mig</sup> (eV)	USPP	0.383 (0.402)	0.565	0.398	0.423 (0.448)
	PAW-PBEsol	0.407 (0.423)	0.633	0.363	0.502 (0.523)
$\nu(THz)$	DFPT	5.018 (6.497)	4.854	7.715	7.844 (7.553)
	FDM	3.873 (2.759)	6.958	8.742	9.712 (4.883)

**Table 5.4:** Migration energies (eV) and attempt frequencies (THz) for vacancy mediated diffusion in elemental fcc/hcp Al and Mg. For hcp systems, the values for basal and (pyramidal) jumps are shown without and (with) parentheses. For DFT settings tags interpretation, refer to the caption in the text and Table 5.1.

**Table 5.5:** Vacancy formation energies and vacancy formation entropies in fcc/hcp Al/Mg systems using different DFT settings. For Al cells, results from regular PAW-PBE functional are also reported.

System	DFT	H <sup>F</sup> (eV)	$S^{F}(k_{\rm P})$	
System	Settings	$\Pi_V(\mathbf{c}\mathbf{v})$	O <sup>A</sup> (KB)	
hcp Mg	USPP	0.755	1.591	
	PAW-PBEsol	0.883	1.968	
fcc Al	USPP	0.582	1.277	
	PAW-PBE	0.690	1.393	
	PAW-PBEsol	0.813	2.324	
fcc Mg	USPP	0.580	0.313	
	PAW-PBEsol	0.893	1.716	
hcp Al	USPP	0.509	0.371	
	PAW-PBE	0.690	1.393	
	PAW-PBEsol	0.710	1.031	



**Figure 5.2:** Atomic hops considered in the diffusion model in hcp (based on the notations in [3]). Top and bottom rows show the basal and pyramidal jumps, respectively. Schematics in the left and right columns represent the solute and vacancy on the same plane (1b) and solute and vacancy on the different plane (1p), respectively. Note that the two reorientation jumps from 1b, that have been treated as a unique jump in previous models, are distinguished by 1b-1b in blue and <u>1b-1b</u> in yellow in the top left figure. Solute and vacancies are indicated by yellow sphere and white square, respectively. Blue spheres represent host atom (modified after [3]).

the accuracy of both transition energies and vacancy formation energies for both systems compared to the USPP. According to the Arrhenius equation in Equation 5.5, the slope of the calculated diffusivity lines corresponds to the activation energy  $E_{act}$  and the intercept with vertical axis corresponds to the diffusion pre-factor  $D_0$ . While the migration energies and vacancy formation energies mainly contribute to the  $E_{act}$ , vacancy formation entropy and migration frequencies mainly influence  $D_0$ . Table 5.6 lists the Arrhenius fit to the selfdiffusivities using different DFT settings and compares those with the values reported in the literature.



**Figure 5.3:** Self diffusion coefficients for fcc Al and hcp Mg. DFT results derived from different exchangecorrelation pseudopotentials and attempt frequency calculation methods are compared with the experimental assessment in reference [12]. For Al systems, diffusivity results with the vacancy formation energy and entropy evaluated from regular PAW-PBE is also shown.

For Al systems, the use of uncorrected PAW-PBE in calculating vacancy formation energy and entropy yield a closer activation energy for diffusion (slope of the diffusivity versus 1/T plot) compared to the experiments. Similar to the reference [129], we find that vacancy formation energy is the dominant contributing factor for the close agreement of DFT-predicted slopes with experiments. Our results show that surface energy correction under-predicts the vacancy formation energies in fcc Al, consistent with previous works [129, 130]. However, migration barriers evaluated from PBEsol are very close to those predicted with PBE. It is important to note that both vacancy formation energy and entropy determine the vacancy concentration term, according to Equation 5.4, and directly contribute to the final diffusion coefficient. Therefore, the choice of XC in free energy calculations at elevated temperatures also has an important impact on the pre-factor term. As shown in Figure 5.3, diffusivities with vacancy formation energies evaluated from PBE yield  $D_0$  intercepts closer to experiments compared to PBEsol. Other factors that can influence the pre-factor term are discussed in detail in Section 5.4.3. A similar effect is found in Mg impurity diffusion in fcc Al as shown in Figure 5.4. The choice of uncorrected PBE XC for vacancy concentration calculations yields the closer diffusivities to the experiments. Table 5.7 lists the Arrhenius fit to the calculated diffusivities for impurity diffusion coefficients and compares these values with the findings from previous works.



**Figure 5.4:** Impurity diffusion coefficients: (a) Mg in fcc Al and (b) Al in hcp Mg. DFT results derived from different exchange-correlation pseudopotentials and attempt frequency calculation methods are compared with the experimental assessment in reference [12]. For Al systems, diffusivity results with the vacancy formation energy and entropy evaluated from regular PAW-PBE is also shown.

Similar to the diffusion in fcc Al systems, PBEsol improves the migration energies compared to USPP for diffusion in hcp Mg systems, leading to the better diffusivity predictions. While PBEsol also improves the vacancy formation energy and entropy compared to USPP, both PBE and corrected PBEsol predicted similar values for vacancy formation energies and entropies. Similar to previous publications [129, 130], we find that vacancy

**Table 5.6:** Arrhenius fit to the calculated self-diffusion coefficients. Diffusivities are fit to the  $D = D_0 \exp(-E_{act}/k_BT)$  equation, where D,  $D_0$ , and  $E_{act}$  are diffusivity, diffusion prefactor and activation energy barrier, respectively. These values are compared to the experimental values reported in the literature, For Al systems, fit to the diffusivity data derived from regular PAW-PBE functional for vacancy formation energies and entropies are also included. For hcp systems, diffusivity values for basal and ( $\vec{c}$ ) are shown without and (with) parentheses. For DFT settings tags interpretation, refer to the caption in the text and Table 5.1.

System	DFT	$D(m^2/s)$	E (eV)	
System	Settings	$D_0(\text{III}/3)$	$\mathbf{L}_{act} (\mathbf{ev})$	
hcp Mg	USPP	5.76E-06 (4.62E-06)	1.14 (1.15)	
	PAW-PBEsol, DFPT	6.15E-06 (7.17E-06)	1.29 (1.30)	
	PAW-PBEsol, FDM	3.99E-06 (3.21E-06)	1.29 (1.30)	
	Assessment [12]	2.88E-05	1.30	
	Ref. [131] (Experimental)	2.00E-04 (2.03E-03)	1.44 (1.46)	
fcc Al	USPP	5.98E-06	1.15	
	USPP(vac:PAW-PBE)	6.71E-06	1.25	
	PAW-PBEsol, DFPT	1.38E-05	1.45	
	PAW-PBEsol, DFPT (vac:PAW-PBE)	5.42E-06	1.32	
	PAW-PBEsol, FDM	2.42E-05	1.45	
	PAW-PBEsol, FDM (vac:PAW-PBE)	9.55E-06	1.32	
	Assessment [12]	1.79E-05	1.32	
	Ref. [132] (Experimental)	9.77E-06	1.27	
fcc Mg	PAW-PBEsol, FDM	1.49E-05	1.26	
hcp Al	PAW-PBEsol, FDM	2.87E-06 (1.92E-06)	1.22 (1.23)	
	PAW-PBEsol, FDM (vac:PAW-PBE)	4.11E-06 (2.76E-06)	1.20 (1.21)	

concentration is less sensitive to the surface energy correction for both self and impurity diffusion in hcp Mg systems. Based on these findings, we use PAW-PBEsol XC functional to calculate the energy barrier in hypothetical phases. For vacancy concentration calculations, we use regular PAW-PBE in systems with Al host atoms and corrected PAW-PBEsol in systems with Mg host atoms.

**Table 5.7:** Arrhenius fit to the calculated impurity diffusion coefficients. Diffusivities are fit to the  $D = D_0 \exp(-E_{act}/k_BT)$  equation, where D,  $D_0$ , and  $E_{act}$  are diffusivity, diffusion prefactor and activation energy barrier, respectively. These values are compared to the experimental values reported in the literature. For Al systems, fit to the diffusivity data where the regular PAW-PBE functional is used to calculate vacancy formation energies and entropies are also included. For hcp systems, diffusivity values for basal and  $(\vec{c})$  are shown without and (with) parentheses. For DFT settings tags interpretation, refer to the caption in the text and Table 5.1.

System	DFT	$D(m^2/s)$	$\mathbf{E}$ (aV)
System	Settings	$D_0(m/s)$	$\mathbf{E}_{act} \left( \mathbf{e} \mathbf{v} \right)$
Al in hcp Mg	USPP	1.17E-05 (1.78E-05)	1.27 (1.31)
	PAW-PBEsol, DFPT	5.12E-05 (7.09E-05)	1.39 (1.43)
	PAW-PBEsol, FDM	9.52E-06 (1.00E-05)	1.39 (1.43)
	Assessment [12]	1.16E-04	1.47
	Ref.[3](DFT)	1.87E-06 (2.02E-06)	1.46
	Ref. [133](DFT)	3.44E-05 (3.11E-5)	1.41
	Ref. [128] (DFT)	4.24E-06 (7.17E-06)	1.29
Mg in fcc Al	USPP	2.06E-05	1.06
	USPP(vac:PAW-PBE)	2.30E-05	1.16
	PAW-PBEsol, DFPT	3.72E-05	1.41
	PAW-PBEsol, DFPT (vac:PAW-PBE)	1.47E-05	1.29
	PAW-PBEsol, FDM	1.45E-05	1.38
	PAW-PBEsol, FDM (vac:PAW-PBE)	5.70E-06	1.25
	Assessment [12]	5.17E-05	1.31
	Ref. [134] (DFT)	-	1.21
Al in fcc Mg	PAW-PBEsol, DFPT	1.03E-05	1.46
Mg in hcp Al	PAW-PBEsol, DFPT	8.58E-06 (1.08E-05)	1.19 (1.20)
	PAW-PBEsol, DFPT (vac:PAW-PBE)	5.04E-06 (6.31E-05)	1.08 (1.10)

### 5.4.3 Effects of attempt frequencies on diffusivities

Next, we study the effect of different attempt frequency calculation methods within quasi-harmonic phonon models. FDM and DFPT methods yield different entropies of vacancy formation and migration, which contributes mainly to the intercept difference ( $D_0$ ) in both self-diffusion and impurity diffusion coefficients. In phonon based QHA, excessive fitting or benchmarking can be avoided as opposed to other methods such as Debye model, where Debye temperature is approximated from experimental data or QHA phonon calculations [129].

Diffusion coefficients derived from both FDM and DFPT approaches are presented in Figures 5.3 and 5.4 and listed in Tables 5.6 and 5.7. DFPT has a better speed-convergence relation due to the direct calculaton of second-order derivatives of the energy compared to the FDM, where the Hessian matrix is obtained via a first order finite-difference small displacement of atoms to compute the forces. Here, we compare the diffusivities derived from DFPT with FDM method. As shown in Figure 5.3 and Table 5.6, FDM calculated phonons yield to a considerably better  $D_0$  values for self-diffusivities in fcc Al compared to the experiments. In case of hcp Mg self-diffusivity, prefactors derived from both FDM and DFPT methods are very close. Therefore, we use the FDM to calculate the attempt frequencies for self-diffusion atomic hops in the hypothetical phases.

Similar analysis is performed for impurity diffusion of Mg in fcc Al and Al in hcp Mg. As illustrated in Figure 5.4 and Table 5.7, prefactors from DFPT and FDM results are similar with slightly better predictions using DFPT in both cases. To be consistent in settings, we implement DFPT method to evaluate the frequency modes for impurity diffusion in the hypothetical phases as it is explained in the next section.

#### **5.4.4** Diffusivity in meta-stable phases

Uncertainty analysis is performed on the self and impurity diffusion calculation of the stable phases of Mg/Al. We find that PAW-PBEsol improves the accuracy of solute/vacancy migration energies. For vacancy formation energy and entropies, regular PAW-PBE performs better than other XC functionals in predicting the diffusion coefficients in Al-based systems. This results in closer activation energy barrier values for diffusion (slope of Figures shown in 5.3 and 5.4) as compared to the values reported in experiments. In terms of prefactor, FDM method is found to perform better in predicting the  $D_0$  intercept for self-diffusivities and DFPT predicts more accurate prefactor values in impurity diffusion cases. Based on these findings, we predict the diffusion coefficients in metastable (hypothetical) cases. Elemental self-diffusivities in hcp Al and fcc Mg, and Al/Mg impurity diffusion in fcc Mg/hcp Al are shown in Figure 5.5 and the Arrhenius fit is listed in Tables 5.6 and 5.7.



**Figure 5.5:** Diffusion coefficients in metastable phases: (a) self-diffusivities in elemental hcp Al and fcc Mg, (b) impurity diffusion of Al in fcc Mg and Mg in hcp Al using the optimized DFT settings identified for stable phases as explained in the text.

#### 5.5 Concluding remarks

As an effort to quantify the uncertainty of diffusion coefficients derived from DFT calculations, we present a study of self and dilute solute diffusion in fcc/hcp-Al/Mg stable and meta-stable phases. We investigate the effect of diffusion model, exchange-correlation functional, and attempt frequency calculation methods on the diffusion coefficients in a quantitative framework. The sixteen-frequency model using the Green's function method is found to predict more accurate diffusivities compared to the previous eight- and thirteenfrequency models. In comparison to the USPP, PAW-PBEsol functional is able to well describe migration energies, vacancy formation energies and entropies, resulting in a more accurate diffusion predictions. In particular, we find that thermalized free energy calculations are more sensitive to the choice of XC and have an important effect on the calculated diffusivities. PBEsol improves the vacancy formation energy and entropy values in Mgbased systems leading to the more accurate activation energy barrier for diffusion, however, it under-predicts the formation energies in Al-based systems. We then study the contribution of different attempt frequency calculation methods through QHA analysis. While the difference between using FDM and DFPT is not as significant as the XC effect, FDM and DFPT are found to better predict the self-diffusivities and solute diffusivities, respectively, by improving the  $D_0$  accuracy compared to the experiments. Finally, we use the optimized settings to evaluate the diffusion coefficients in meta-stable phases. Present work explains the factors that play a role in diffusivity calculations from first-principles. Calculated diffusion data in stable and meta-stable phases can be used to improve CALPHAD diffusion mobility databases for Mg/Al alloys [135]. The method explained in this work can be readily applied to the self and impurity diffusion prediction in other fcc/hcp systems.

# Chapter 6: Solute/Twin boundary interaction as a new atomic-scale mechanism for Dynamic Strain Aging: Interstitial diffusion

Strength and formability are critical properties for the hexagonal close packed materials and can consequently be improved by controlling twin nucleation and growth. In this chapter, we study the effect of alloying elements on strain rate and temperature dependence of twin growth. Without using any fitting parameters, we derive an analytical model which takes atomic scale calculated parameters as input and predicts the equilibrium concentration of segregated solutes and strengthening due to solute-twin interactions. This model predicts the strain-rate/temperature conditions of negative strain rate sensitivity in titanium, under loading conditions that favor twinning, with oxygen interstitial. The predictions are in quantitative agreement with available experiments. Our findings present a new mechanism for dynamic strain aging as a result of solute segregation to the twin boundaries.

#### 6.1 Introduction

Dynamic strain aging (DSA) is usually associated with an increase in the strength of an alloy due to the diffusion of solutes around dislocations that temporarily hinder dislocation motion. At the macroscopic scale, DSA is often manifested by serrations in the stress-strain curves and Portvein-LeChatelier (PLC) deformation bands, indicative of local instabilities, which arise when DSA renders the strain rate sensitivity of the material negative [136,

137, 138, 139]. Strain rate sensitivity is defined as the change in the strength of material  $\tau$  versus the change in strain rate  $\dot{\epsilon}$ ,  $m = \frac{\Delta \tau}{\Delta \log \dot{\epsilon}}$ . Negative strain rate sensitivity (nSRS) has detrimental effects on processing and formability of metallic alloys. As such, understanding the mechanisms underlying the nSRS is crucial for improving the mechanical properties and predictive alloy design.

The DSA model by Curtin *et al.* introduced the "cross-core" diffusion of solutes in the dislocation core as the atomic scale mechanism of DSA in Al-Mg alloys [140]. During this process, the solutes in the vicinity of the dislocation core migrate from the tensile to the compressive sides (or vice versa depending on the solute misfit volume), during periods where dislocations are stopped by other obstacles. The driving force for this mechanism is the large disparity in the solute/dislocation interaction energy in tension and compression sides within the core of a dislocation. Also, the lower energy barrier for solute transport within the core compared to bulk, accelerates the kinetics of cross-core diffusion, leading to the DSA.

Most of the research on DSA has been done on cubic systems [141, 142, 143, 144, 145, 146, 147, 148], however, DSA has been observed in hexagonal close packed (hcp) metals such as Magnesium (Mg) and Titanium (Ti) alloys as well [26, 149, 150, 151, 152, 153, 154, 155]. Unlike in cubic structures, the slip systems in hcp crystals involve Burgers vectors of different lengths–  $\langle a \rangle$  and  $\langle c+a \rangle$ – with a large critical stress differential to activate on basal, prismatic and pyramidal planes. In addition, twinning is a major mode of deformation in these systems. While the "cross-core" diffusion can occur in hcp metals as well, an analysis of the experimental work in Mg and Ti alloys suggest that other mechanisms for DSA may exist in hcp crystals. For instance, DSA has been observed in Mg-rare earth (RE) alloys with very low solute concentrations. This level of concentration cannot achieve

the strength levels needed to predict the experimentally observed stress drops (5-10 MPa depending on the alloying element) [23, 24, 25]. In addition, DSA has been observed in single crystals oriented in favor of twinning in Ti. Akhtar *et al.* performed tensile tests on single crystal Ti samples with oxygen as the main interstitial content and observed the appearance of serrated stress-strain curves at a temperature of about 423 K and a strain rate of  $1.66 \times 10^{-4} \,\mathrm{s^{-1}}$  in the test with twin-favored orientation [6]. Their microstructure observations revealed that the { $10\overline{1}2$ } twins were indeed the main deformation mode with only a small amount of slip lines in the vicinity of twins. This observation suggests that the interaction of solutes with the twin boundary (TB) can offer an alternative mechanism for DSA. Other experimental studies have also observed DSA in different metallic alloys, in the presence of interstitial solutes, and with active twinning deformation modes [26, 144, 149, 150, 151, 152, 153, 154, 155, 156]. These studies found nSRS with increasing number of twins, which highlights the important link between DSA and the microstructure and connect solute/boundary– in addition to solute/dislocation interactions– to DSA.

Here we propose an "in-twin", analogous to the "cross-core", mechanism for DSA. We focus on the  $(10\overline{1}2)$  twin boundary, which is observed in all hcp metals and was particularly operative in the work of Akhtar *et al.* [6]. First principles calculations have shown a strong interaction between solutes and this twin boundary [54, 58, 89, 90, 92, 157]. In addition, solute segregation to the attractive sites and the subsequent inhibition of twinning have been experimentally observed in the work of Nie *et al.* [106].

First, we note that there are important similarities between the solute/dislocation and solute/twin boundary interactions as follows. For both substitutional and interstitial solutes, there are repulsive and attractive interaction sites, with a large difference in interaction energies, similar to the energy difference between tension/compression sides within

a dislocation core. The difference in interaction energy, creates a driving force for solute transport near the twin boundary. This underlying feature is common between both substitutional and interstitial solutes, however, here we focus on the interstitial mechanism for direct comparison with the available experimental results of Akhtar *et al.* on oxygen in Ti. Furthermore, we have shown previously that the migration barrier of oxygen interstitials in the vicinity of the twin boundary is significantly reduced [157]. The reduced barrier for transport within the "core" of the defect is the second common feature between the "cross-core" and the "in-twin" diffusion mechanisms. At low plastic shear strain rates, twin boundaries grow via individual nucleation and growth events. During the waiting time between individual nucleation/growth events, solutes can diffuse from the repulsive sites to the attractive sites within the twin boundary region at a faster rate than bulk. This local segregation pins the twin boundary and larger stress levels are needed for subsequent growth. After an increase in the applied shear stress, the twin boundary can grow at a faster rate until further hardening. This can manifest macroscopically as DSA or serrated flow. We quantify the competition between twin growth rate and oxygen diffusion in Ti, using first principles calculations and show that the "in-twin" diffusion is a viable mechanism that explains experimental serrated stress-strain curves on Ti single crystals where twinning is the dominant deformation mode.

The rest of this chapter is organized as follows. Section 6.2 contains the computational details. Theoretical framework of strengthening model and the solute effects on different twin growth modes are explained in Section 6.3. Finally, model predictions and the following discussion are presented in Section 6.3.3.

# 6.2 Computational method

Density functional theory (DFT) calculations are performed with VASP [95] using the projector augmented wave (PAW) method [120] within the generalized gradient approximation (GGA) exchange-correlation functional as determined by Perdew and Wang [32]. A cut-off energy of 500 eV, and the Methfessel-Paxton smearing method (ISMEAR =1) is applied with SIGMA=0.15 in all DFT calculations. We use double twin geometry with 10 atomic layers between twin boundaries and total number of 240 Ti atoms to maintain the periodicity along all three directions (cf. Figure 6.2). The dimension of the supercell employed for DFT calculations is chosen to be  $13.72 \times 8.76 \times 33.85$  Å along X : [1011], Y :  $[1\overline{2}10]$  and Z :  $(10\overline{1}2)$  directions, respectively. To maintain the dilute limit of solutes, thickness of at least 3a; a = 2.92 Å along Y :  $[1\overline{2}10]$  is required as it is implemented in these calculations. Single periodic unit of twin boundary plane with a dimension of 6.86 × 2.92 Å along X and Y directions is used to evaluate the diffusion coefficients following the recently developed methodology [157]. These settings combined with the choice of  $3 \times 4 \times 1$  k-mesh guarantees ~ 0.1 eV/atom error in the accuracy of site energies. Site energy for each interstitial site is defined as the difference between the energy of the supercell with oxygen at an interstitial site and that of the reference, the cell with "bulk-like" octahedral sites located furthest from both twin boundaries. All atomic positions within the relaxed box dimensions of the reference cell are allowed to relax until the forces are smaller than  $10 \text{ meV}\text{Å}^{-1}$ .

Transition barrier energies are calculated using climbing-image nudged elastic band (CI-NEB) method [96, 97] with constant cell size and one intermediate image. The force criterion for NEB convergence is set to be 20 meVÅ<sup>-1</sup>. Attempt frequency for the interstitial solute transitions  $\nu$ , is derived using the Vineyard's equation [98] within the transition

state theory as,  $v = \frac{\prod_{i=1}^{3N} v_i}{\prod_{i=1}^{3N-1} v'_i}$ , where  $v_i$  and  $v'_j$  are stable normal mode frequencies at the local energy minimum and saddle point states, respectively. Finite difference small displacement method is used to compute the Hessian matrix from which the normal mode frequencies are derived [99, 100].

The interaction between oxygen solutes and twinning dislocation, or disconnection, is studied using DFT with the corresponding simulation cell shown schematically in Figure 6.5(a). Twinning disconnection consisting of a dislocation and a step character is constructed following the procedure explained in [58]. Dislocation is imposed by applying the anisotropic displacement field of the dislocation character with a Burgers vector of 0.62 Å[55, 158]. This cell has the dimension of 99.36 × 8.76 × 60 Å along X : [ $\overline{1011}$ ] and Y : [ $1\overline{210}$ ] and ( $10\overline{12}$ ) normal direction, respectively and contains 2550 atoms. Simulation cell is slightly rotated along Y dislocation line direction to maintain the periodicity of twin boundary at each side of the disconnection along X. A vacuum layer with thickness of 15 Å is imposed at top of the cell to avoid interaction images between the planes. The system is then relaxed using  $1 \times 4 \times 1$  *k*-mesh while fixing the atoms within 10 Å of the cell along Z direction fixed. The rest of DFT settings are the same as ones explained above for coherent twin boundary calculations.

#### 6.3 Theory of solute effects on Twin Growth

Twin growth in hcp Ti occurs by nucleation and glide of twinning dislocations or disconnections [159, 160, 161]; line defects with both a step and a dislocation character. An entirely new twin can be created from a free surface [162, 163], from a defect with a large local stress concentration, dislocation-twin interactions[164, 165, 166, 167, 168], twin-twin interactions [169, 170] and precipitation/void induced interactions [171]. Several mechanisms for twin nucleation and growth have been proposed in the literature from both computational and experimental prospects. Recently, Capolungo and Taupin [172] employed molecular dynamics simulations to study the thickening mechanism of twin by the nucleation of disconnection loops from existing ledges on the twin interface. This type of twin nucleation mechanisms are commonly observed experimentally as discussed by Hirth et al. [173]. Another study by Fan and El-Awady [174] revealed nucleation of twin and basal-toprism (BP) facets as a result of (near) c-axis tension using molecular dynamics simulation. Heterogenous nucleation and growth of the twins from the presence of defects, such as dislocations, has been also extensively investigated [74, 76, 175, 176]. In a recent in-situ tension experiment study, dislocation slip induced twin growth is characterized [177]. The authors identified the formation of twin inclinations comprising of BP facets and observed the growth of twin through extension of BP interface length with no evidence of longitudinal growth/glide. While each set of above studies address how twin nucleates or grows from an already nucleated twin, any aspect of thermal activation or the role of solutes on the twin nucleation and thickening requires more in-depth analysis.

Here, we use the recent model of Luque *et al.* for growth of hcp twin boundaries, where twin growth occurs by the thermally activated nucleation and expansion of a twinning dislocation loop– or island formation– on existing twin boundaries [178]. Figure 6.1 (a)-(b) shows schematically the formation of a twin loop according to the model proposed by Luque *et al.* Assuming an existing twin boundary, applied stress provides the driving force for the nucleation of a new twin dislocation loop. As the nucleated loop expands, the twin boundary advances by a unit step height.



**Figure 6.1:** Twin growth by formation of a square twinning dislocation loop: (a)-(b) show the lateral growth of twin by island formation. (a) is the cross-section of twin loop and (b) is the view normal to the twin boundary. (c)-(e) show the twin growth where the solutes can segregate to and pin the boundary (c). Upon applying a large enough stress, the twin boundary can escape the solute environment and grow by forming a new loop (d). If the solutes can diffuse fast enough to reach the new twin boundary, this process can repeat (e). Red atoms indicate the interstitial solutes and the dashed lines are twin boundaries.

On the other hand, presence of solutes affects the energetics of twin growth, as discussed in [178]. Particularly, segregation of solutes to the boundary significantly increases the energy barrier for subsequent nucleation of the loop. Therefore, growth of twin boundaries at a constant rate, requires a higher level of applied stress. Upon applying a large enough stress, the twin boundary can escape the solute environment and grow by forming a new loop. As the boundary moves further, solutes may catch up by diffusing to the shifted twin boundary. If the solutes can diffuse fast enough to reach the new twin boundary, this process can repeat, similar to the dislocation-based DSA. Therefore, the competition between twin growth rate and diffusion of solutes around the boundary determines the dynamic nature of this mechanism. Figure 6.1(c)-(e) demonstrates this process schematically.

Following [178], the total energy to nucleate a twin loop of size  $L \times L$  where solutes segregate to the TB is:

$$\Delta E = 4\gamma L - \tau b_{tw} L^2 + \Delta E^{\text{seg}}$$
(6.1)

where  $\gamma$  is the energy cost per unit length of the twin loop with the twinning Burgers vector of  $b_{tw}$ .  $\tau$  is the applied stress and  $\Delta E^{\text{seg}}$  is the additional energy change due to the solute segregation from the repulsive to the attractive sites.

Figure 6.2 shows the geometry of the  $(10\overline{1}2)$  twin boundary, with layers L0, containing two attractive octahedral sites O1 and O2, and L1, containing two repulsive octahedral sites O3 and O4. Previous DFT calculations found the interaction energy of an oxygen interstitial in sites O1, O2, O3, O4, O5 and O6 to be -0.082 eV, -0.096 eV, 0.145 eV, 0.054 eV, -0.050 eV and -0.071 eV, respectively. These interaction energies are defined as the difference between the energy of an oxygen atom at each site and that of an oxygen atom in a bulk octahedral site. Beyond L1, bulk geometry is retrieved and the twin/solute interaction energy becomes negligibly small.

Oxygen atoms at each of the octahedral sites can jump into two octahedral sites at the adjacent layer, through intermediate metastable sites thereby creating four distinct octahedral to octahedral (O-O) jumps between L0 and L1 layers. Figure 6.2 shows the minimum energy path within each O-O jump. In a previous work, we identified new tetrahedral interstitial sites close to the twin boundary which provide the lowest-barrier-path for an oxygen atom during O3  $\rightarrow$ O1, O3  $\rightarrow$ O2 and O4  $\rightarrow$ O1 jumps. The minimum energy path for the remaining O4  $\rightarrow$ O2 jump involves a hexahedral site as shown in Figure 6.2.



**Figure 6.2:** Twin boundary geometry and minimum energy paths for oxygen segregation. Oxygen atoms at the octahedral, crowdion, tetrahedral and hexahedral sites are shown by the symbols O, C, T and H, respectively. The arrows show the minimum energy path for oxygen atom jumps from octahedral sites in L1 layer to the lowest energy octahedral sites at the TB, L0 resulting in the segregation. Labels for the sites located behind octahedral sites are indicated in the parenthesis.

barriers corresponding to these jumps are calculated using NEB method and are presented in Figure 6.3.



**Figure 6.3:** (a) Position of *all* stable oxygen interstitial sites around  $(10\overline{1}2)$  twin boundary. Octahedral, crowdion, tetrahedral and hexahedral sites are shown by the symbols O, C, T and H, respectively. (b)-(e) relative energy barriers corresponding to the different possible paths between octahedral sites from L1 to L0. Transport occurs via meta-stable interstitial sites. Each of the meta-stable sites is indicated with a scatter symbol and the peak between each two symbol corresponds to the transition state energy derived from the nudged elastic band calculations.

Next, we derive an analytical expression for the additional stress exerted on a twin boundary by segregation of solutes via "in-twin" diffusion. The magnitude of this additional stress depends on the degree of segregation and therefore the kinetics of the "in-twin" diffusion. To obtain a closed form solution for this additive, time-dependent strength, we make some simplifying assumptions following Curtin *et al.* 's treatment of the "crosscore" diffusion. First, we define the driving force for the jumps as the average binding energy difference between the repulsive and attractive sites,  $\overline{\Delta W}$ . Next, we define the energy barrier for an "average" O-O jump as follows. Let us name the forward transition energy barrier and attempt frequency in the direction of the driving force, from L1 to L0,  $\Delta H^{\text{fw}}$  and  $v^{\text{fw}}$  and the backward energy barrier and attempt frequency as  $\Delta H^{bw}$  and  $v^{bw}$ , where  $\Delta H^{\text{fw}} + \overline{\Delta W} = \Delta H^{bw}$ . The forward jump rate is proportional to  $v^{\text{fw}}e^{-\beta\Delta H^{fw}}$  and the backward jump rate is proportional to  $v^{\text{bw}}e^{-\beta\Delta H^{bw}}$  with  $\beta$  equals  $1/k_BT$  where  $k_B$  is the Boltzmann constant and T is the temperature. First, given the small difference between the forward and backward attempt frequencies, we consider  $v^{\text{fw}} = v^{\text{bw}} = v_0$ . We then define the forward and backward rates for an "average" O-O jump as  $\Gamma^{\text{fw}} = v_0 e^{-\beta(\Delta H^{\text{ave}} - \overline{\Delta W}/2)}$  and  $\Gamma^{\text{bw}} = v_0 e^{-\beta(\Delta H^{\text{ave}} + \overline{\Delta W}/2)}$  where  $\Delta H^{ave}$  is a reference transition barrier obtained by averaging the forward and backward energy barriers. Note that detailed balance requires the ratio of forward to backward jumps to be proportional to  $e^{\beta \overline{\Delta W}}$ , and these jump rates satisfy this condition.

Having two distinct octahedral sites in each layer and considering two L1 layers on each side of the boundary, the transition rate from L0 to L1 becomes  $\Gamma_{L0\to L1} = 8\Gamma_0 e^{\beta \overline{\Delta W}/2}$  where the reference transition rate  $\Gamma_0 = v_0 e^{-\beta \Delta H^{ave}}$ . Similarly, the transition rate from L1 to L0  $\Gamma_{L1\to L0} = 8\Gamma_0 e^{-\beta \overline{\Delta W}/2}$ . Taking the average between forward and backward energy barriers, as shown in Figure 6.3, we use a  $\Delta H^{ave}$  value of 1.496 eV and a  $v_0$  of 13.7 THz.

Solute concentration in layers L0 and L1 should satisfy the master equation:

$$\dot{c}_{L0}(t) = \Gamma_{L1 \to L0} c_{L1}(t) - \Gamma_{L0 \to L1} c_{L0}$$

$$\dot{c}_{L1}(t) = \Gamma_{L0 \to L1} c_{L0}(t) - \Gamma_{L1 \to L0} c_{L1}$$
(6.2)

where the dot symbol represents time derivative. The solution to the above system of differential equations with initial values of  $c_{L0} = c_{L1} = c_0$  yields the closed form concentration change in  $L_0$  as follows:

$$\Delta c_{L0} = c_{L0}(t) - c_0 = c_0 \tanh\left(\frac{\beta \overline{\Delta W}}{2}\right) \left[1 - e^{-16\cosh\left(\frac{\beta \overline{\Delta W}}{2}\right)\Gamma_0 t}\right]$$
(6.3)

The additional energy change due to solute transport from layer L1 to L0 is then given by:

$$\Delta E^{\text{seg}} = \Delta c_{L0} N_{L_0} \overline{\Delta W} \tag{6.4}$$

where  $N_{L_0}$  is the number of possible sites in layer L0. For a twin loop of area  $L^2$ ,  $N_{L_0} = L^2/\Sigma$ with  $\Sigma$  being the twin boundary area per atom. Following the formalism of [178] for the energy required for loop nucleation in the presence of segregated solutes, we have:

$$\Delta E = 4\gamma L - \tau b_{tw} L^2 + \Delta \tau_s b_{tw} L^2 \tag{6.5}$$

where  $\Delta \tau_s$  is the pinning stress exerted on the twin boundary by the segregated solutes. Substituting Equation 6.4 into Equation 6.1 and comparing with Equation 6.5 leads to the following expression for the time dependent  $\Delta \tau_s$ :

$$\Delta \tau_s(t) = \frac{1}{b_{tw} \Sigma} \Delta c_{L_0}(t) \overline{\Delta W}$$
(6.6)

Substituting  $\Delta c_{L_0}(t)$  from Equation 6.3 into the above equation yields final additive strengthening caused by solute segregation to the TB as a function of time:

$$\Delta \tau_s(t) = \frac{1}{b_{tw} \Sigma} \left[ c_0 \overline{\Delta W} \tanh\left(\frac{\beta \overline{\Delta W}}{2}\right) \left[ 1 - e^{-16 \cosh\left(\frac{\beta \overline{\Delta W}}{2}\right) \Gamma_0 t} \right] \right]$$
(6.7)

# 6.3.1 Role of solutes on disconnection glide

The model explained above, assumes that once a twin loop is formed, it can easily expand by glide of the bounding twinning disconnections, leaving a new twin boundary to which the solutes can then migrate. The underlying assumption is that, for a segregated existing twin boundary, the lateral twin growth mode – nucleation of a new twin loop– dominates the longitudinal growth mode by glide of disconnections. These two growth modes



**Figure 6.4:** Twin growth modes: (a) lateral growth of twin from state (1), fully segregated coherent twin boundary (green dashed line), to state (2), twin loop nucleation (green solid line) and (b) Longitudinal growth of twin disconnection from the fully segregated state: (a) migration of disconnection from state (1), fully segregated solutes to the boundary (green dashed line), to state (2), disconnection glide represented for a single periodic unit (green solid line). Color coding shows the common neighbor analysis (CNA) [13]. White atoms have hcp coordinate while black atoms show the defective region. Solutes are colored as red atoms.

are shown in Figure 6.4. To identify the dominant mechanism, we compare two critical stress values needed to accommodate each growth mode from fully segregated boundary. The larger of two values will dictate the dominating mechanism.

In the lateral growth case, presented in the previous section, the critical stress for twin loop nucleation is:

$$\tau_{\rm lat} = \frac{\Delta E_{\rm lat} N_{L_0}}{b_{tw} \Sigma L^2} = \frac{\Delta E_{\rm lat}}{b_{tw} \Sigma}$$
(6.8)

where  $\Delta E_{\text{lat}}$  is the critical energy barrier for twin loop nucleation. This energy barrier is the difference between the state (1), where solutes are fully segregated to the favorable sites at the coherent twin boundary and the state (2), where solutes colored with bright red are no longer at the boundary upon twin loop nucleation. These sites are in fact located at a layer below the nucleated boundary as shown in Figure 6.4(a). The energy cost for this transition

is computed by associating the segregated state (1) to the O1 and O2 and the state (2) to O5 and O6 site energies in the coherent twin boundary cell, respectively (cf. Figure 6.2). According to the values reported earlier,  $\Delta E$  between state (1) and (2) would be the sum between the energy difference of O1  $\rightarrow$  O6 and O2  $\rightarrow$  O5 which is equal to 0.0574 eV.

To obtain the critical stress for the longitudinal growth, first we need to determine if oxygen interstitials prefer to segregate to the step (core of the defect) rather than the twin boundary sites. To this end, we study the interaction between solutes and twin disconnection using direct DFT calculations. Note that these are expensive calculations, involving 2550 atoms. Figure 6.5 shows the simulation set up and the possible octahedral positions for oxygen interstitials near the disconnection. We find that oxygen atoms are attracted to the boundary at S1, S3 and S6 with the calculated site energies of -0.092 eV, -0.068 eV and -0.042 eV, respectively. However, it is energetically unfavorable for oxygen to be at S2, S4 and S5; oxygen, placed at each of these sites relaxes to nearby attractive site by pushing the boundary. This proves the lack of oxygen to segregate to the step part of the disconnection.

Given the effect of time and temperature, solutes can diffuse and segregate to the twin boundary where there is a strong attractive binding. Segregation to these attractive sites pins the twin boundary and inhibits the further growth until a critical value of extra stress is applied. Twin growth mode is accompanied by either (a) lateral growth by forming a new twin loop on the boundary, or (b) longitudinal growth by glide of twin disconnection along the boundary.

For the longitudinal growth, stress as a function of energy change is given by:

$$\tau_{\rm long} = \frac{\Delta E_{\rm long} N_{L_0}}{b_{tw} \xi l_{tr}} = \frac{\Delta E_{\rm long}}{b_{tw} \Sigma}$$
(6.9)



**Figure 6.5:** Solute interaction with twinning disconnection: (a) shows the DFT simulation cell set up comprising of coherent twin boundary connected by twin disinclination and (b) shows the twinning disconnection with a step and dislocation character and possible octahedral interstitial sites for oxygen near the disconnection. Color coding shows the common neighbor analysis (CNA) [13]. White atoms have hcp coordinate while black atoms show the defective region.

where  $\Delta E_{\text{long}}$ ,  $\xi$ , and  $l_{tr}$  are the critical energy barrier for longitudinal twin growth mode, dislocation line length and the distance twin disconnection front traverses, respectively. With the glide of twinning dislocation from fully segregated state, solutes indicated with red color would be located at a layer below the extended boundary (cf. Figure 6.4(b)). This transition costs the same amount of energy as in the case of lateral growth mode, leading to the same critical stress for both growth modes. With  $\Sigma = 10.07 \frac{\text{Å}^2}{\text{atom}}$ ,  $l_{tr} = 6.86 \text{ Å}$ ,  $\xi = 2.92 \text{ Å}$ , and  $b_{tw} = 0.62 \text{ Å}$  for Ti, critical stress needed for activating each twin growth mode would be  $\tau_{\text{long}} = \tau_{\text{lat}} = 1.47 \text{ GPa}$ . This indicates that disinclination glide is not inhibited by the solutes segregation to the boundary, therefore twin growth is controlled by the nucleation of twin loops.

#### 6.3.2 Assessing the waiting time

The degree of segregation, and consequently the amount of additional strength due to segregation, is a function of the waiting time  $t_w$  between individual nucleation and growth events. If the solute diffusion is fast enough, the solutes can catch up with the moving twin boundary and trap the boundary again. Therefore, the dynamic nature of this process is determined by the competition between twin growth rate and the diffusion rate of solutes.

The twin growth rate *R* is defined as the time derivative of the total thickness of twin *H*. Assuming, twinning as the only deformation mode, the total plastic strain  $\epsilon$  is given by:

$$\epsilon = N_{\rm tw} \gamma_{\rm tw} \tag{6.10}$$

where the number of twin dislocations is  $N_{tw} = H/h$  with h and  $\gamma_{tw} = b_{tw}/h$  denoting the characteristic step height and the plastic shear strain associated with a single twin dislocation respectively. Taking the derivative of Equation 6.10, with respect to time, leads to the relation between twin growth rate and strain rate as follows:

$$R = \frac{\dot{\epsilon}h}{\gamma_{tw}} \tag{6.11}$$

For a solute diffusivity of D towards the boundary, the waiting time  $t_w$  should then satisfy

$$\sqrt{Dt_w} = Rt_w \tag{6.12}$$

Substituting Equation 6.11 in Equation 6.12 relates the waiting time and the strain rate as

$$t_w = \frac{D\gamma_{tw}^2}{h^2 \dot{\epsilon}^2} \tag{6.13}$$

Finally, evaluating equation Equation 6.7 at  $t = t_w$  gives the change in strengthening as a function of strain rate and temperature.

#### 6.3.3 Model Predictions

We use the equations developed in the previous section to predict the additive strengthening generated from interstitial oxygen segregation to the TB in Ti. Using the site and transition energies calculated in [157], we get an average binding energy  $\overline{\Delta W} = 0.18 \text{ eV}$ and average energy barrier of  $\Delta H^{\text{ave}} = 1.496 \text{ eV}$ . In addition, we use the diffusivity tensor, derived for oxygen diffusion near the TB from first-principle calculations in [157], and take the component corresponding to diffusion towards the boundary in the evaluation of  $t_w$  according to Equation 6.13. This value is  $D = D_0 \exp(-E_{\text{act}}/k_BT)$  with  $D_0 = 1.348 \times 10^{-7} \text{ m}^2/\text{s}$  and  $E_{\text{act}} = 1.313 \text{ eV}$  and is higher than bulk diffusion as discussed in [157]. With  $\Sigma = 10.07 \frac{\text{Å}^2}{\text{atom}}$ ,  $\nu_0 = 13.7 \times 10^{12} \text{ s}^{-1}$ ,  $b_{\text{tw}} = 0.62 \text{ Å}$ , h = 3.11 Å, and  $\gamma_{tw} = 0.2$  for Ti, and the above driving force and transition barrier energies, the additive strengthening due to the "in-twin" diffusion is evaluated.

Figure 6.6 shows the additive strength, predicted by Equation 6.7, as a function of strain rate. At low strain rates, where twin growth is slow, the boundary experiences an additional pinning stress exerted by the segregated solutes. If the applied stress is lower than this value, the boundary remains trapped and twin growth is suppressed. The value of this strength depends on the total oxygen content, as shown in Figure 6.6(a) for several grades of commercially pure Ti. If the temperature is held constant, but strain rate is increased, at a critical strain rate, the strength will drop to zero, indicating that the twin growth rate is now faster than solute diffusion and the boundary can escape the segregated solutes and grow without additional stress. This critical strain rate, depends on the temperature as well. With increasing temperature, the diffusion rate becomes comparable to a given twin growth rate. Figure 6.6(b) shows the effect of temperature on the strain-rate-dependence of strength.

In addition, we compare the model predictions with experimental observations of Akhtar *et al.* [6]. The initial concentration of 0.05at% is chosen for direct comparison with that work. Single crystals of Marz grade Ti (with 0.05at% oxygen), favorably oriented for  $\{10\overline{1}2\}$  twinning, were deformed at temperatures between 78 K and 773 K. The serrations in stress-strain curves appeared at the temperature of 423 K and a strain rate of  $1.66 \times 10^{-4} \text{ s}^{-1}$ . Their microstructure observations confirmed the  $\{10\overline{1}2\}$  twinning as the main deformation mode with only a small amount of slip lines in the vicinity of twins. As shown in Figure 6.6 (a) our predictions for the onset of DSA is consistent with the experimental conditions.



**Figure 6.6:** Variation of strength with strain rate at various temperatures and initial oxygen content in Ti. (a) shows prediction of present model at T=423 K for various oxygen contents and (b) shows the strength predictions at various temperatures. Dashed vertical lines show the experimental strain rate reported in [6].

In summary, we have presented a new mechanism for dynamic strain aging as a result of solute interactions with twin boundaries. Specifically, the solute strengthening, resulting from the twin growth impediment by solute segregation, can cause DSA and nSRS. Previous theories attributed the DSA only to the solute/dislocation interactions while the connection between solute segregation to twin boundaries and DSA has never been considered. This mechanism provides a physical justification of experimentally observed PLC bands when high amount of twin activity is observed [6, 24, 25, 153, 179, 180, 181, 182]. We show that the atomic-scale mechanism for DSA from solute/twin interaction depends only on a few fundamental material properties which can be calculated via first principles calculations. Without any fitting parameters, the present model makes accurate predictions of the physical conditions necessary for DSA, compared to relevant experiments. In addition, it is important to set the context for applicability of this model as it does not deal with the impurity drag effect on the grain boundary motion as discussed in Cahn and Luck and Stuwe et al. model [183, 184]. Solute drag on grain boundaries or dislocations occurs when the exerted force by impurity atmosphere around the boundary/dislocation changes the boundary/dislocation's mobility at constant stress. This phenomenon is important during recrystallization and creep [185, 186]. However, in the present case, we study the strengthening effect of solutes by calculating the additional stress required to keep the same boundary mobility -or twin growth rate- as the solutes segregate to the boundary. While at extreme conditions- very low or very high strain rates or temperature- twins remain either "loaded" with the solutes or "breakaway" from the solutes, under certain mechanical conditions within a continuous transition region between the extreme cases, solutes can catch up, lock and diffuse to the boundary. We postulate that this is the underlying mechanism responsible for serrated flow observed with twinning as the dominant deformation mode. Our model provides a framework for Ti and other hcp alloys where twin activity is observed and solute segregation to the twins are favored. Theory presented in this work and the corresponding findings lead to a more comprehensive understanding of DSA, particularly in hcp systems.

# Chapter 7: Solute/Twin boundary interaction as a new atomic-scale mechanism for Dynamic Strain Aging: Vacancy-mediated diffusion

This chapter focuses on extending the dynamic strain aging model developed for interstitial solutes to the substitutional solute interactions with the twin boundaries. Using a numerical solution approach, we solve the master equation of vacancy-mediated solute diffusion to predict the equilibrium concentration of segregated solutes and strengthening due to solute/twin interactions. This model predicts the strain-rate and temperature dependence of negative strain-rate sensitivity and that dynamic strain aging in Mg under the conditions where twinning is an active deformation mode. Our findings present a new mechanism of dynamic strain aging as a result of substitutional solute segregation to the twin boundaries.

# 7.1 Introduction

In the previous chapter, we introduced the interstitial solutes effect on the twin nucleation and growth mechanisms in hexagonal close packed (hcp) materials. Without using any fitting parameters, we developed an analytical model to predict the equilibrium concentration of segregated solutes and strengthening due to interstitial solute/twin interactions from atomic scale calculated parameters. Here, we extend our model to studying the effect of substitutional solutes on the twin growth. In the vacancy-assisted solute diffusion, the solute atom moves into a vacancy located next to it. If vacancies are not available, a vacancy needs to be created next to the solute. Therefore, the activation energy for this diffusion mechanism is the sum of the vacancy formation energy and the migration barrier for solute/vacancy jump. This diffusion mechanism is also a thermally activated process. Additionally, accurate capturing of the correlated random walk in vacancy-mediated diffusion has been recognized as a complex task in the literature [105].

The goal here is to study the occurrence of dynamic strain aging (DSA) as a result of substitutional solutes segregation to the twin boundary in hcp alloys. We use first-principles density functional theory (DFT) calculations to study the interaction of technologically important Al and Gd solutes with ( $10\overline{1}2$ ) twin boundary (TB) in Mg. Section 7.2 contains the computational details. In Section 7.3, DSA theory of twin boundary strengthening is extended for substitutional solutes and compared with the solute/dislocation strengthening. Section 7.4 focuses on explaining the formulations and theory of thermodynamics and kinetics of solute/twin boundary interaction energy, solute/dislocation interaction energy, solute/vacancy binding and activation energy barriers. Finally, we use these formulations and evaluated values in Section 7.4 and Gd solutes in Mg and compare these results with the solute/dislocation interaction for Al and Gd solutes in Mg and compare these results with the solute/dislocation interaction models. The proposed model is also applicable to other hcp materials, such as Ti alloys.

#### 7.2 Computational Methods

First-principles calculations are performed with VASP [95] using projector augmented wave (PAW) method within the generalized gradient approximation (GGA) [120]. We use Methfessel-Paxton smearing of 0.15 eV and a plane wave cut-off of 350 eV. A double twin boundary geometry, with 10 atomic layers between the twin boundaries and 240 Mg atoms,
is considered to maintain the periodicity along all three directions. To maintain the dilute limit of solutes, thickness of at least 3a; a = 3.19 Å along Y :  $[1\bar{2}10]$  is required as implemented in these calculations. The twin boundary supercell used in DFT calculations is presented in Figure 7.1 which has a dimension of  $15.16 \times 9.57 \times 37.80$  Å along X :  $[\bar{1}011]$ , Y :  $[1\bar{2}10]$  and Z :  $(10\bar{1}2)$  directions. These settings combined with the choice of  $3 \times 4 \times 1$ *k*-mesh guarantees ~ 0.1 eV/atom error in the accuracy of site energies. For each substitutional site, site energy is defined as the difference between the energy of the supercell with two solutes positioned at the symmetrically equivalent sites near the boundary and that of the reference; the cell with two solutes located at the "bulk-like" sites at the furthest distance from both twin boundaries. Solute/vacancy pairs binding energies are calculated within the first nearest neighbor shell of the vacancies. All atomic positions within the relaxed box dimensions of the reference cell are allowed to relax until the forces are smaller than  $10 \text{ meV} \text{Å}^{-1}$ . Spin-polarization is enabled to consider magnetism calculations in the Gd contained simulations.

Solute/vacancy transition barrier energies are calculated using climbing-image nudged elastic band (CI-NEB) method [96, 97] with constant cell size and one intermediate image. Three and five intermediate images are considered for some of the paths in Gd containing alloys for faster convergence. The force criterion for NEB calculations is set to be 20 meVÅ<sup>-1</sup>. Attempt frequency for the solute transitions *v*, is derived using the Vineyard's equation [98] within the transition state theory as,  $v = \frac{\prod_{i=1}^{N} v_i}{\prod_{i=1}^{N-1} v_i}$ , where  $v_i$  and  $v'_j$  are stable normal mode frequencies at the local energy minimum and saddle point states for the considered *N* number of atoms, respectively. Finite difference small displacement method calculation up to the third nearest neighbor of solute/vacancy pairs is used to compute the Hessian matrix from which the normal mode frequencies are derived [99, 100].

To compare the change in solute/vacancy transition energy barrier near to the dislocation core with that of bulk, energy minimization at 0 K is employed. Empirical potential based calculations are performed using LAMMPS package [52] and an embedded atom method (EAM) potential for Mg/Al [15]. Since there is no available interatomic potential for Mg/Gd, we only consider Mg/Al alloy dislocation core calculation. A cylinder with the dimensions of X = 800 Å, Y = 800 Å,  $Z = \xi = 16.5$  Å and the dislocation line direction aligned along Z and Burgers vector *b* along X is incorporated.  $\langle a \rangle$ -type basal edge dislocation in Mg is introduced by displacing all the atoms according to the anisotropic displacement field of the dislocation [55, 56]. Fixed boundary conditions along X and Y and periodic along line direction Z is used, respectively. According to the potential cut-off, atoms within the outer 50 Å thickness of the cylinder are fixed. The possible sites for substitutional Al near one of the cores and the relaxed core structure of dissociated partials are depicted in Figure 7.2 and Figure 7.3, respectively.

Cross-core transition barrier energies are calculated using NEB method with multiple replicas of a system within LAMMPS. Parallel NEB calculation based on the interpolated ideal positions with Kspring of 1 eV/Å and the force criterion of 10 meV/Å is employed to find the saddle point for each solute/vacancy jump within the dislocation core. These values are also compared with the transition barrier energies of solutes within the bulk.

#### 7.3 Theoretical model of DSA

#### 7.3.1 Solute/twin boundary interaction model

Here, we derive an analytical expression for the additive stress exerted on a twin boundary due to the segregation of substitutional solutes via vacancy-mediated "in-twin" diffusion. This additional strength is dependent on the degree of segregation as well as the kinetics of vacancy-mediated diffusion of solutes to the boundary. In the previous chapter, we derived a closed form solution for the time dependent concentration change due to the interstitial solute segregation to the boundary. Due to the close values of the site energies for the interstitial positions within each layer and the small variations in the solute atomic jump energy barriers, the general master equation system was reduced to a simple ordinary differential equation which has a closed form solution. This simplified assumption, however, is no longer valid in a general case where both repulsive and attractive sites exist within each layer. As it will be illustrated later, due to the vacancy formation energy contribution in the energy barrier of solute transitions toward/from the boundary in substitutional solute segregation cases, the variation between the solute atomic jump energy barriers cannot be ignored. To incorporate the explicit contribution of each transition individually in the master equation solution, we follow a numerical approach as explained below.

Having *n* distinct possible sites for the solutes, transition jump from site *i* to *j* is defined as  $\Gamma_{i \to j} = v_0 e^{-\beta[\Delta H^{i \to j} + \Delta W^{i \to j}]}$  where  $v_0$ ,  $\Delta H^{i \to j}$ , and  $\Delta W^{i \to j}$  are attempt frequency, transition energy barrier and site energy difference (driving force), respectively.  $\beta$  is  $\frac{1}{k_B T}$  where  $k_B$  and *T* are Boltzmann constant and temperature, respectively. Solute concentration at each site as a function of time  $c_i(t)$  should satisfy the general master equation as follows:

$$\dot{c}_{i}(t) = \sum_{j=1, j \neq i}^{n} \Gamma_{j \to i} c_{j}(t) - c_{i}(t) \sum_{j=1, j \neq i}^{n} \Gamma_{i \to j}$$
(7.1)

where the dot symbol represents time derivative. Each of the contributing sites in the vacancy-mediated solute segregation is treated individually which leads to a system of n first order differential equation. The forward and backward driving forces, transition energy barriers and attempt frequencies are each explicitly distinguished in the above formulation.

Starting from initial solute concentration of  $c_0$  at each site, we assess the governing system of differential equations numerically as there is no analytical closed form solution for such a system. Referring to the derivations in Section 6.3, the time dependent additional strengthening due to the solute segregation is:

$$\Delta \tau_s(t) = \frac{1}{2b_{\rm tw} \Sigma} \Delta c(t) \, \Delta W \tag{7.2}$$

where  $\Delta c(t)$  and  $\Delta W$  are the numerically evaluated concentration change in the attractive site on the twin after time *t* and the driving force (binding energy) for the segregation to this attractive site, respectively. Factor of one-half is due to the fact that half of the sites at the boundary are attractive for the solutes, as it will be shown in Section 7.4.3.  $b_{tw}$  and  $\Sigma$  are the Burgers vector for twinning dislocation and the twin boundary area per atom, respectively.

Similar to the interstitial solute segregation to the twin boundary, the degree of segregation is a function of waiting time  $t_w$ , between individual nucleation and growth events. The competition between solute diffusion and the growth rate of twin, which is strain-rate dependent, governs the dynamic nature of this process. The trap event can occur when the solutes diffuse fast enough to catch the moving twin boundary preventing it from further growth. Further increase in the strain-rate can breakaway the boundary from solutes. This process can repeatedly occur leading to the dynamic strain aging. Similar to the interstitial diffusion explained in Section 6.3.2,  $t_w$  can be derived as follows:

$$t_w = \frac{D\gamma_{\rm tw}^2}{h^2 \dot{\epsilon}^2} \tag{7.3}$$

where D,  $\dot{\epsilon}$ , and  $\gamma_{tw} = b_{tw}/h$ , are the diffusion coefficient, strain-rate and the plastic shear strain associated with a single twin dislocation with  $b_{tw}$  and h as the twinning dislocation Burgers vector and step height of twinning dislocation, respectively. Finally, evaluating Equation 7.2 at  $t = t_w$  gives the change in strengthening as a function of strain-rate and temperature.

## 7.3.2 Solute/dislocation interaction model

To compare the additional strengthening due to solute/twin boundary interaction with solute/dislocation, we employ the cross-core DSA model developed by Curtin *et al.* [140]. The proposed formulations have been incorporated for face centered cubic based metals. After adjusting this method for hcp based metals and modifying the geometrical parameters, the additional strengthening as a result of solute/dislocation interaction in hcp is derived, which has a similar form to that of fcc and follows this equation:

$$\Delta \tau_s(t) = \alpha (2c_0 \overline{\Delta W} / \sqrt{3}b^3) \tanh\left(\frac{\beta \overline{\Delta W}}{2}\right) \left[1 - e^{-6\cosh\left(\frac{\beta \overline{\Delta W}}{2}\right)\Gamma_c t}\right]$$
(7.4)

where  $\alpha = \frac{\langle \Delta W(x-w/2) - \Delta W(x+w/2) \rangle_x}{\Delta W}$  within the dislocation core width of w. b,  $\overline{\Delta W}$  and  $\langle \rangle_x$  denote the dislocation Burgers vector, average binding energy for cross-core diffusion in the dislocation core width and the average over the range of dislocation positions where the initial strength  $dE_0(x)/dx$  is maximized. Here, we consider the upper-bound of additive strengthening term using  $\alpha = 1$ .  $\Gamma_c$  is the reference transition rate and defined as  $\Gamma_c = \overline{\nu_0}e^{-\beta\overline{\Delta H_c}}$  with  $\overline{\nu_0}$  and  $\overline{\Delta H_c}$  defined as the average attempt frequency and transition energy barrier for cross-core solute diffusion. The waiting time of solute/dislocation trap events is defined as  $t_w = \Omega/\dot{\epsilon}$  following the notations in [140], where  $\Omega$  correlates with the mobile

 $\rho_m$  and forest  $\rho_f$  dislocation densities by  $\Omega = \rho_m b / \sqrt{\rho_f}$ . The term  $\Omega$  is both strain and temperature dependent and can be measured experimentally.

### 7.4 Effect of Al and Gd solutes on DSA in Mg

In this section, we investigate the thermodynamics and kinetics of solute segregation to the (1012) twin boundary and  $\langle a \rangle$ -type basal dislocation in Mg. Al, Mn, Zn, and some of the rare earth elements such as Gd have been found to increase the ductility of Mg, and therefore are widely used as alloying elements in Mg. The commonly used AZ31 Mg alloy shows a strong strain-rate dependence on the room temperature ductility [187]. It has been also shown that addition of Al and Gd elements to Mg changes the strain-rate sensitivity (SRS) in this metal [23, 24, 25, 153, 154, 188, 189, 190]. Previously, Stanford *et al.* performed tensile tests on Mg-0.90at% Al and Mg-0.24at% Gd at strain-rates between  $10^{-4} - 10^{-1}$  l/s and up to the deformation temperature of 300 °C. While no occurrence of DSA had been observed in Mg-Al, Mg-Gd exhibited negative strain-rate sensitivity (nSRS) at 200 °C and 250 °C. The authors attributed this different behavior between Al and Gd containing Mg alloys to the solute/dislocation interactions. However, this mechanism could not explain the reason why DSA has occurred in Gd-containing, but not Al-containing alloy as there is a considerable attractive binding between solutes and dislocation in both of these alloys. Microstructure analyses in this work showed that Gd-containing alloy exhibited extensive deformation twinning at 200 - 250 °C where DSA was also observed while no mechanical twin had been identified in Al-containing alloy. This observation suggests that the interaction of solutes with the twin boundary can offer an alternative mechanism for

DSA. Other experimental works also evidenced nSRS in Mg alloys with various concentrations of Al at room temperature within the strain-rate range of  $10^{-5} - 10^{-1}$  1/s where twin activity was also observed [153, 154, 188, 189].

Here, we propose the solute/twin boundary segregation, analogous to the "cross-core" solute diffusion around the dislocation core, as a responsible mechanism for DSA in substitutional alloys [140, 191]. We compare the effects of dislocation and twin boundary interaction with solutes at different concentrations. DFT is employed to compute site energies, vacancy/solute bindings and energy barriers at different sites near/at the TB. Since it is computationally challenging to directly calculate solute/dislocation interaction energies with DFT, we use the analytical model developed by Yasi *et al.* in [192] to evaluate interaction energies and validate the values using empirical potential calculations. Finally, we use the equations developed in the previous section with the DFT driven inputs to predict the additive strengthening due to the solute segregation to the TB and compare the results quantitatively with the strengthening due to the "cross-core" DSA mechanism.

### 7.4.1 Solute/vacancy binding near the twin boundary

Figure 7.1 shows the twin boundary geometry within a double twin boundary supercell, possible substitutional sites near the boundary and the paths for vacancy/solute transitions. The thermodynamic driving force for a solute jump from site *i* to *j* is governed by the difference between the site energies,  $\Delta W^{i \rightarrow j} = E_j - E_i$ . Since the simulation cell contains two twin boundaries in order to maintain the periodicity, site energy is defined as the difference between energy of supercell with two solutes located at the particular site and the supercell with two solutes positioned at the bulk-like sites with a maximum distance from both twin boundaries divided by two.



**Figure 7.1:** (1012) twin boundary geometry in Mg, possible substitutional sites and the paths between solute/vacancy jumps for (a) Al and (b) Gd. Green arrows show the jumps in the direction of attractive solute/twin boundary binding driving force and red arrows show the repulsive binding energy. Solutes tend to move in the direction of attractive thermodynamic binding. Attractive sites for the solutes are underlined in the figure.

Substitutional solutes transport through the vacancy-mediated diffusion. To calculate activation energy barrier for diffusion, we need to evaluate vacancy formation energies for each site around the twin boundary, binding energy between solute and vacancy and the migration energy barrier for each jump. In order the assess the first two, we followed the vacancy formation energy and binding energy formulations for bulk as explained in [193] and developed the corresponding expressions to evaluate vacancy formation and solute/vacancy binding energies around the twin boundary. The migration energy barrier is calculated using NEB. Two sets of symmetrically equivalent solute/vacancy pairs at each

boundary are considered to calculate the energies due to having two twin boundaries within a supercell. Vacancy formation energy for a site at/near the TB can be computed as follows:

$$E_{vf} = \frac{1}{2} \Big[ E(Mg_{N-2}V_2) - (N-2)E_{\frac{\text{bulk}}{\text{atom}}} - 2E_{\text{TB}}A_{\text{TB}} \Big]$$
(7.5)

where  $E(Mg_{N-2}V_2)$ ,  $E_{\frac{\text{bulk}}{\text{atom}}}$ ,  $E_{\text{TB}}$  and  $A_{\text{TB}}$  are the energies corresponding to the supercell with two vacancies located at the symmetrically equivalent sites within each boundary, atomic energy of bulk Mg, twin boundary energy per area and the area of the twin boundary plane, respectively. N denotes the number of atoms in the cell. Knowing that the twin boundary energy is  $E_{\text{TB}} = \frac{E(\text{double twin cell}) - N E_{\frac{\text{bulk}}{4000}}}{2A_{\text{TB}}}$ , vacancy formation energy can be simplified to the following form:

$$E_{vf} = \frac{1}{2} \Big[ E(Mg_{N-2}V_2) + 2E_{\frac{\text{bulk}}{\text{atom}}} - E(\text{double twin cell}) \Big]$$
(7.6)

The binding energy between the solute and vacancy  $E_{\text{bind}}^{\text{sol/vac}}$ , can be calculated using the following expression:

$$E_{\text{bind}}^{\text{sol/vac}} = \frac{1}{2} \Big[ E(Mg_{N-4}V_2X_2) + E(\text{double twin cell}) - E(Mg_{N-2}X_2) - E(Mg_{N-2}V_2) \Big]$$
(7.7)

where  $E(Mg_{N-4}V_2X_2)$ , E(double twin cell),  $E(Mg_{N-2}X_2)$  and  $E(Mg_{N-2}V_2)$  are the energy of supercell with two symmetrically equivalent vacancies and solutes near/at each boundary, energy of pure double twin boundary cell without any vacancy and solute, energy of supercell with two solutes and energy of supercell with two vacancies, respectively. Using the information above, the activation energy for diffusion would be:

$$Q = E_{vf} + E_{\text{bind}}^{\text{sol/vac}} + E_{\text{mig}} = \frac{1}{2} \Big[ E(Mg_{N-4}V_2X_2) + 2E_{\frac{\text{bulk}}{\text{atom}}} - E(Mg_{N-2}X_2) \Big] + E_{\text{mig}}$$
(7.8)

where  $E_{\text{mig}}$  is the migration barrier for the solute/vacancy jump evaluated using NEB calculations.

# 7.4.2 Solute/vacancy binding near the dislocation

Solute/vacancy binding and activation energy barrier around the dislocations follows the similar formalism as explained for twin case. All dislocation calculations are performed with the classical potentials. Since the simulation cells contain only one dislocation as compared to the double boundary simulation cells, equations in Section 7.4.1 are modified for one solute (cf. Section 7.2). For the case of solute/dislocation interactions, vacancy formation energy, solute/vacancy binding energy and activation barrier follows below expressions:

$$E_{vf} = E(Mg_{N-1}V_1) - \frac{(N-1)}{N}E_{Mg_N}^{\text{undisl}} - E_{\text{dislocation}}$$
(7.9)

$$E_{\rm dislocation} = E_{Mg_N}^{\rm disl} - E_{Mg_N}^{\rm undisl}$$
(7.10)

$$E_{bind}^{sol/vac} = E(Mg_{N-2}V_1X_1) + E_{Mg_N}^{disl} - E(Mg_{N-1}X_1) - E(Mg_{N-1}V_1)$$
(7.11)

$$Q = E_{vf} + E_{bind}^{sol/vac} + E_{mig} = E(Mg_{N-1}V_1) + \frac{1}{N}E_{Mg_N}^{undisl} - E_{dislocation} + E(Mg_{N-2}V_1X_1) - E(Mg_{N-1}X_1) + E_{mig}$$
(7.12)

where  $E_{Mg_N}^{\text{undisl}}$ ,  $E_{Mg_N}^{\text{disl}}$ ,  $E_{\text{dislocation}}$ ,  $E(Mg_{N-2}V_1X_1)$ ,  $E(Mg_{N-1}V_1)$ ,  $E(Mg_{N-1}X_1)$  and  $E_{mig}$  are the energy of the pure supercell with N number of Mg atoms, energy of the pure supercell with an edge dislocation, excess energy of the cell due to the dislocation core, energy of a supercell with one solute and one vacancy in the core, with one vacancy in the core, with one solute in the core, and solute/vacancy migration barrier, respectively.  $E_{\rm dislocation}$  can be computed by directly subtracting the energy per atom of N atom Mg supercell with edge dislocation from the un-dislocated cell. Note that the binding energy (driving force) here is calculated by subtracting the energy of a supercell with a solute at each of the sites near the dislocation core (shown in Figure 7.4) from a cell with solute far from the core (bulk-like) region. The bulk values are derived by considering the sites and the corresponding jumps far from the dislocation core, for the sake of comparison.

### 7.4.3 Model predictions

Using DFT calculations and employing the formulations derived in previous section, we calculate the thermodynamic driving force due to the solute/twin boundary binding and the kinetic activation energy barrier for vacancy-mediated diffusion of Gd/Al solutes jumps near the TB. Table 7.1 and Table 7.2 list all these values along with the attempt frequencies corresponding to each jump for Al and Gd solutes in Mg, respectively. The binding energies and activation energy barriers for diffusion within the basal and along the pyramidal directions are also included for comparison. These energy calculations show that there is a large driving force for solute segregation to the twin boundary for both Al and Gd solutes. NEB calculations also indicate that jumps toward the twin boundary have lower energy barriers compared to the jumps in the bulk suggesting the kinetic feasibility of solutes segregation to the TB. DFT calculations show that Al solutes are attracted to site 1 while repelled from site 2. Gd solutes, however, are attracted to site 2, with a larger binding energy compared to the Al case, and repelled from site 1. We also find that for the P4 solute/vacancy pair jump, Gd solutes are not stable at site 1 and therefore this jump always occurs in the opposite direction. Similarly for P6 solute/vacancy settings, while Gd

solutes are stable at site 1, no energy barrier exists for the solutes to jump to the site 2. Thus, this transition always occurs in the direction of P6 with no energy barrier leading to the site 2 segregation.

It is important to note that the key parameter in the strengthening effect due to twin segregation mechanism is the binding energy term  $\Delta W$  while the activation barrier controls the strain-rate dependency. To avoid simplifying assumptions, contributions from both forward and backward jumps are considered explicitly in the DSA formalism as explained in Section 7.3.1. To evaluate the waiting time term, we use bulk diffusion of Gd and Al in Mg as reported in [126]. Tensorial average of anisotropic diffusion along the basal  $D_{\text{basal}}$  and prism  $D_{\text{prism}}$  planes has been calculated and used in Equation 7.3. All the necessary inputs for the twinning strengthening calculations are listed in Table 7.3.

DSA has been observed in Mg-RE alloys with very low solute concentrations, however previous dislocation based DSA models were not able to predict the experimentally measured stress drops for such low concentrations (10 – 30 MPa depending on the alloying element) [23, 24, 25, 188, 194]. Here, we compare the strengthening contribution and DSA from solute/twin boundary segregation with the solute/dislocation segregation. The term  $\Omega$ which correlates the waiting time to the strain-rate is both strain and temperature dependent and can be measured experimentally. We use the  $\Omega$  value measured from the work by Dini *et al.* where the dislocation densities at 190 °C for a AZ91D cast alloy are reported [195].

It is computationally challenging to calculate the solute/dislocation binding energies and activation energy barriers for cross-core diffusion, which are necessary inputs for DSA model, using DFT. As such, we evaluate interaction energies using the interaction model introduced by Yasi *et al.* [192]. Based on this theory, the solute/dislocation interaction energy has contributions from the interaction of solute misfit strain with the dislocation stress

**Table 7.1:** Al solute/twin boundary binding (driving force), vacancy formation energy added to the solute/vacancy binding, migration energy barriers, activation enthalpies and the attempt frequencies for the jumps into/within the twin boundary in Mg evaluated from DFT, respectively. Energy values are reported in eV and the attempt frequencies are in THz. Forward-fw (backward-bw) values correspond to the jumps in the direction (opposite direction) of the arrowheads in Figure 7.1. Basal and pyramidal jumps within the bulk values are also included for comparison. Negative values show the attractive binding.

		$E_{\rm vf} + E_{\rm bind} \ ({\rm eV})$	$E_{\rm mig}~({\rm eV})$	Q (eV)	$v(\times 10^{12} \mathrm{THz})$
Path	Binding energy (eV)	(fw)	(fw)	(fw)	(fw)
		(bw)	(bw)	(bw)	(bw)
D1	0.010	0.637	0.998	1.635	21.584
Γ I	0.010	0.637	1.012	1.649	18.524
D2	0 123	0.870	0.412	ev)       Q (eV)         i)       (fw)         i)       (bw)         ii)       (bw)         ii)       (bw)         ii)       (bw)         ii)       (bw)         iii)       (bw)         iii)       (bw)         iii)       (bw)         iii)       (bw)         iii)       (bw)         iii)       (cv)         iiiii) <th(cv)< th="">      &lt;</th(cv)<>	6.998
Γ∠	0.125	0.652	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	4.318	
D2	0 122	0.847	0.405	1.251	4.817
FS	0.155	0.691	$\begin{array}{c ccccc} V) & E_{\rm mig} ({\rm eV}) & Q ({\rm eV}) \\ \hline & ({\rm fw}) & ({\rm fw}) \\ \hline & ({\rm bw}) & ({\rm bw}) \\ \hline & 0.998 & 1.635 \\ 1.012 & 1.649 \\ 0.492 & 1.649 \\ 0.412 & 1.282 \\ 0.432 & 1.084 \\ 0.405 & 1.251 \\ 0.429 & 1.120 \\ 0.467 & 1.054 \\ 0.429 & 1.120 \\ 0.467 & 1.054 \\ 0.467 & 1.054 \\ 0.432 & 1.169 \\ 0.484 & 1.044 \\ 0.398 & 1.163 \\ 0.666 & 1.198 \\ 0.562 & 1.438 \\ 1.955 & 2.529 \\ 1.898 & 2.774 \\ 0.500 & 1.286 \\ 0.514 & 1.286 \\ 0.650 & 1.431 \\ 0.651 & 1.432 \\ \end{array}$	1.346	
D/	0 117	0.586	0.467	1.054	7.462
Γ4	-0.117	0.737	0.432	1.169	4.619
D5	0 127	0.560	0.484	1.044	5.933
FJ	-0.127	0.765	0.398	1.163	7.143
D6	0.250	0.532	0.666	(fw) (bw) 1.635 1.649 1.282 1.084 1.251 1.120 1.054 1.169 1.044 1.163 1.198 1.438 2.529 2.774 1.286 1.286 1.431 1.432	1.993
FU	-0.230	0.876	0.562	1.438	1.908
D7	0.250	0.574	1.955	(fw) (bw) 1.635 1.649 1.282 1.084 1.251 1.120 1.054 1.169 1.044 1.163 1.198 1.438 2.529 2.774 1.286 1.286 1.431 1.432	41.404
Г/	-0.230	0.875	1.898	2.774	186.535
D	0	0.786	0.500	1.286	7.158
r <sub>basal</sub>	0	0.771	0.514	1.286	6.463
D	0	0.782	0.650	1.431	17.636
r <sub>pyr</sub>	0	0.781	0.651	1.432	21.375

**Table 7.2:** Gd solute/twin boundary binding (driving force), vacancy formation energy added to the solute/vacancy binding, migration energy barriers, activation enthalpies and the attempt frequencies for the jumps into/within the twin boundary in Mg evaluated from DFT, respectively. Energy values are reported in eV and the attempt frequencies are in THz. Forward-fw (backward-bw) values correspond to the jumps in the direction (opposite direction) of the arrowheads in Figure 7.1. Basal and pyramidal jumps within the bulk values are also included for comparison. Negative values show the attractive binding.

		$E_{\rm vf} + E_{\rm bind} \ ({\rm eV})$	$E_{\rm mig}~({\rm eV})$	Q (eV)	$v(\times 10^{12} \mathrm{THz})$
Path	Binding energy (eV)	(fw)	(fw)	(fw)	(fw)
		(bw)	(bw)	(bw)	(bw)
D1	0.017	0.842	0.821	1.662	3.303
Γ I	-0.017	0.812	0.860	1.672	9.090
D7	0.274	0.772	0.109	$\begin{array}{ccccc} (eV) & Q (eV) \\ w) & (fw) \\ w) & (bw) \\ \hline & & & \\ \hline \hline & & \\ \hline & & \\ \hline \hline & & \\ \hline & & \\ \hline & & \\ \hline & & \\ \hline \hline \hline & & \\ \hline \hline & & \\ \hline \hline \hline \\ \hline \hline \hline \hline$	4.148
Γ∠	-0.274	0.884	0.541		6.176
D2	0.201	0.924	$E_{mig}$ (eV)Q (eV)(fw)(fw)(bw)(bw)0.8211.6620.8601.6720.1090.8810.5411.4250.2771.2010.6691.484 $\infty$ $\infty$ 00.2350.1710.7820.1030.51300.8720.7431.4011.9492.8002.7753.3400.2471.0910.2231.0920.2971.1370.2971.139	1.201	2.873
F 3	-0.291	0.816		2.398	
D/	0.252	0.487	$\infty$	$\infty$	N/A
Γ4	0.232	0.235	0	0.235	N/A
D5	0.260	0.611	0.171	0.782	0.829
гJ	0.209	0.409	0.103	0.513	0.978
D6	0 543	0.872	0	0.872	1.680
FU	-0.545	0.659	0.743	1.401	9.681
D7	0 543	0.851	1.949	2.800	N/A
Г/	-0.545	0.564	2.775	3.340	N/A
D	0	1.091	0.247	1.091	5.294
r <sub>basal</sub>	U	1.092	0.223	1.092	6.690
D	0	1.137	0.297	1.137	3.059
r <sub>pyr</sub>	0	1.139	0.297	1.139	1.135

Quantity	Description	Al	Gd	Unit
а	Lattice constant (pure Mg)	3.19	3.19	Å
С	$\vec{c}$ (pure Mg)	5.19	5.19	Å
$b_{ m tw}$	Burgers vector (pure Mg)	0.480	0.480	Å
h	Step height (pure Mg)	3.78	3.78	Å
$c_0$	Initial concentration	0.90	0.24	at%
Σ	Twin boundary area per atom	$12.1 \times 10^{-20}$	$12.1 \times 10^{-20}$	$\frac{m^2}{atom}$
$D_{ m basal}^{ m bulk}$	Diffusivity (basal)	$0.50 \exp(-1.47/k_BT)$	$0.44 \exp(-1.31/k_BT)$	$cm^2/s$
$D_{ m prism}^{ m bulk}$	Diffusivity (prism)	$0.60\exp\left(-1.50/k_BT\right)$	$0.42\exp\left(-1.33/k_BT\right)$	$cm^2/s$

**Table 7.3:** Numerical values used for evaluating DSA from twin segregation model formulated in Equation 7.2 for Al and Gd solutes in Mg.

**Table 7.4:** Numerical values used for evaluating DSA from solute/dislocation interaction model formulated in Equation 7.4 for Al and Gd solutes in Mg.

Quantity	Description	Al	Gd	Unit
b	Burgers vector (basal edge)	3.19	3.19	Å
$c_0$	Initial concentration	0.90	0.24	at%
$\overline{\Delta W}$	Average binding energy	0.163	0.287	eV
$\Omega[195]^{1}$	Strain/Temp dependent quantity	0.0022	N/A	—
$\frac{\Delta V}{V}$ [14]	Volumetric strain misfit	-0.355	0.622	—
$E_{I_2}[14]$	Solute/ I <sub>2</sub> SFE	-0.034	-0.095	eV
<sup>1</sup> at 190° C				

field as well as the solute/ $I_2$  basal edge dislocation stacking fault energy (SFE). These terms are evaluated and reported in [14] for a range of solutes in Mg. Following the notations and values in [14], Gd/Al solute interaction energies with basal edge dislocation in Mg are calculated as shown in Figure 7.2. The maximum binding energy within the cores is the maximum difference between the interaction energy in the compression side and the tension side of the dislocation stress field. These values are also plotted in Figure 7.2 and listed in Table 7.4.



**Figure 7.2:** Solute/dislocation interaction energies and the difference between the interaction energies at the compression and the tension sides of basal edge dislocation core for (a,c) Al and (b,d) Gd in Mg calculated using the analytical model explained in [14]. Al (smaller than Mg) and Gd (larger than Mg) solutes tend to reside in the compression and tension sides of dislocation core, respectively.

Similar to the binding energy calculations, transition barrier energies for the cross-core diffusion around the dislocation core are challenging to be assessed using DFT. Here, we simply use the DFT evaluated transition energy barriers and attempt frequencies in bulk as presented in Table 7.1 and Table 7.2 for Al and Gd solutes, respectively.

To compare how the energy barrier of solute/vacancy jumps near the core is compared to the bulk, we use 0 K energy minimization combined with NEB to model the basal edge dislocation in Mg and to calculate the cross-core energy barriers within the core. We only present the results for Mg/Al case as there is no empirical potential currently available in the literature for Mg/Gd. Figure 7.3 shows the Nye tensor analysis on the basal edge dislocation core of Mg using the Liu EAM potential [15]. The possible sites for solutes within the core and paths for solute/vacancy jumps are illustrated in Figure 7.4. Solute/dislocation binding energies, vacancy formation energies, solute/vacancy binding energies and migration energies for each path are also calculated following the expressions explained in Section 7.4.2 and the results are reported in Table 7.5. As the results show, the barrier for cross-core jumps is about ~ 0.3 eV lower than solute/vacancy jump at bulk suggesting that the cross-core diffusion is kinetically favorable around the core. Also, the larger driving force for cross-core jumps compared to the jumps within the compression (and tension) sides of the dislocation highlights the importance of cross-core jumps in solute trap and eventually DSA.

Finally, the additional strengthening due to the solute/twin boundary and solute/dislocation interactions are evaluated. According to the Table 7.1 and Table 7.2, segregation to the attractive sites at the TB is controlled by "in-twin" jumps labeled as P6. We use the energetics and attempt frequencies of this jump and other DFT evaluated inputs in Equation 7.2 to predict solute/twin boundary additional strengthening. Figure 7.5 shows the additional strengthening as a function of strain-rate for solute segregation to the twin boundary and dislocation at different temperatures for Mg-0.90*at*% Al and Mg-0.24*at*% Gd alloys. As it is shown, stress drop values in the twinning segregation is comparatively larger than the dislocation core segregation. This finding suggests that the previously reported discrepancies between the experimentally measured stress drops and the dislocation DSA theories is due to dismissing the contribution of twin segregation effect on DSA at low solute concentrations.



**Figure 7.3:** Nye tensor analysis on the basal edge dislocation core of Mg using Liu [15] empirical potential at 0 K. (a) shows the edge component and (b) shows the screw component of the dissociated partials, respectively.

The implications of DSA as a result of substitutional solute segregation to the twin boundary are as follows. At very low strain-rates, solutes diffuse toward the TB and exert pinning stress to the boundary. Hence, at the applied stresses lower than this value, solutes remain segregated to the boundary. As the strain-rate increases up to a critical point at a given temperature, twin growth rate exceeds the diffusion rate of solutes, thereby the boundary "breakaways" from the solutes cloud and the strength drops to zero. Temperature also effects this process; with increasing temperature, solutes diffuse at higher rates. The



**Figure 7.4:** Cross-core diffusion of Al in Mg basal edge dislocation evaluated using empirical potential molecular statics. Possible substitutional sites around the dislocation core and the paths between them are illustrated. Paths (1) and (2) denote cross-core jumps and the (3) and (4) denote within the compression and tension sides of core, respectively.

higher diffusivity values, comparable to the twin growth rate, leads to the solute/TB trap events to occur at higher strain-rates.

It is important to note that some of the input parameters in the proposed model need to be rectified before interpreting the results and comparing with experiments. The diffusion coefficients used in the above predictions correspond to bulk diffusion, however the considerable decease in migration barrier and stronger driving force near the boundary suggests higher diffusivity in presence of boundary. Increase (decrease) in diffusion coefficients shifts the strengthening plots to the right (left) along the strain-rate axis. Accurate prediction of onset of DSA requires calculating the diffusivities in presence of the twin boundary. Moreover, in the dislocation model [140],  $\Omega$  term is one of the key parameters in assessing the waiting time and this value has not been measured for Gd solutes in Mg.

**Table 7.5:** Al solute/dislocation binding (driving force), vacancy formation energy added to solute/vacancy binding, migration energy barrier and activation barrier enthalpy for the solute jumps evaluated with empirical potential calculations. All energy values are reported in eV. Forward-fw (backward-bw) values correspond to the jumps in the direction (opposite direction) of the arrowheads in Figure 7.4. Basal and pyramidal jumps within the bulk values are also included for comparison. Negative values show the attractive binding.

Path	Binding energy	$E_{\rm vf}$ + $E_{\rm bind}$	$E_{\rm mig}$	Q
		(fw)	(fw)	(fw)
		(bw)	(bw)	(bw)
P1	-0.140	2.199	0.15	2.349
		2.386	0.11	2.496
P2	-0.143	2.184	0.19	2.374
		2.380	0.14	2.520
P3	-0.001	2.064	0.55	2.614
		2.075	0.54	2.615
P4	0.003	2.357	0.19	2.547
		2.379	0.16	2.539
P <sub>basal</sub>	0	2.386	0.22	2.606
		2.380	0.23	2.610
$P_{\rm pyr}$	0	2.380	0.28	2.660
		2.376	0.28	2.656

This parameter should also be evaluated accurately to be able to interpret the DSA due to the solute/dislocation interaction. Additional experimental analysis particularly on single crystals, where the deformation mode is restricted to the twinning, is also envisioned to directly compare the model predictions with experiments.

In summary, we present a new mechanism for the dynamic strain aging as a result of substitutional solute interactions with the twin boundaries. Without the use of any fitting parameters, the present model can be used to predict the equilibrium solute concentration at the segregated sites and the physical conditions necessary for DSA due to the substitutional solutes/twin boundary interactions. All of the key materials and inputs for the



**Figure 7.5:** Additional strengthening due to the solute/twin boundary interaction (solid lines) compared to the solute/dislocation interaction (dotted lines) for (a) Mg-0.90*at*% Al and (b) Mg-0.24*at*% Gd. Change in the additional strengthening at the given strain-rate and temperature demonstrates the dynamic strain aging mechanism.

proposed model can be evaluated from atomistic simulations and in particular from firstprinciples calculations. This framework can be also used to predict nSRS and DSA as well as strengthening in other hcp alloys.

#### **Chapter 8: Conclusion and Future Directions**

#### 8.1 Summary of Results

The overarching goal of this dissertation is to understand fundamental reasons underlying different twinning behavior of various hexagonal close packed (hcp) metals by comparing twin nucleation and growth mechanisms in these systems. Of particular interest is the effect of alloying on twin nucleation and growth in Ti and Mg alloys.

A systematic framework is developed to study the interaction of dislocations with symmetrical tilt grain boundaries in Ti using MEAM calculations.  $\langle a \rangle$ -type dislocation interaction with ( $\overline{1}011$ ) and ( $\overline{1}013$ ) generated the corresponding twinning dislocations on each boundary.  $\langle c \rangle$  and  $\langle c + a \rangle$  dislocations interaction with ( $\overline{1}011$ ) created  $\langle a \rangle$ -type slip on the basal planes in the neighboring grain. In addition to these defects, ( $10\overline{1}2$ ) twin embryo has been nucleated from  $\langle c \rangle$  and  $\langle c + a \rangle$  dislocation interaction with ( $\overline{1}013$ ). Additional applied shear stress causes further growth of the nucleated ( $10\overline{1}2$ ) embryo. These findings reveal new mechanisms of heterogenous twin nucleation and growth as a result of dislocation / grain boundary interactions.

We extended the above framework to model the role of strain transfer in activation of deformation twinning from general grain boundaries. Experimental observations have shown that, despite the good alignment of grain pairs in favor of twinning, twin has not been nucleated as a result of slip in the adjacent grain. To further study the perquisite conditions for slip-induced twin activation, we modeled a random grain boundary characterized by our experimental collaborators. EBSD and TEM observations confirmed that despite the high CRSS necessary for twin activation in the hard oriented grain,  $\langle a \rangle$  slip on prismatic plane in the soft grains led to the pyramidal slip rather than twinning. We incorporated MEAM calculations to study the interaction of  $\langle a \rangle$ -type prismatic loop interaction with the characterized random grain boundary. Consistent with experimental observations, our simulations also revealed the pyramidal-I slip activity in the neighboring grain. Upon applying shear strain, additional defects are nucleated; a 3D BP facet and basal cross slip within the hard grain. Nucleation of BP facets, which has been found to play an important role in nucleation and growth of (1012) twins, under the applied stress primarily suggests the possibility of twinning at sufficiently large local stress levels. This also suggests that the distribution of local grain-level stress may be quite different from the macroscopic applied stress, thus causing the grain to suppress twinning.

Next, we used DFT to study the effect of oxygen (O) alloying on (1012) twinning in Ti. First, we identified and calculated all possible interstitial sites for O at and around twin boundary. We then calculated the migration energies for solute jumps between different sites. Finally, using an exact solution to the master equation for diffusion, we quantified the diffusivity of O near the twin boundary. Our results predicted enhanced mobility of O near the twin boundary, presenting the kinetic feasibility of oxygen segregation to the twin boundary and further pinning effect leading to the suppression of twinning. The proposed framework enables the prediction of large-scale diffusivity quantity near twin boundaries, or any symmetrical grain boundary in general, from accurately evaluated first-principles inputs at the atomic scale. Systematic uncertainty analyses have been also performed to quantify the variations in diffusivity predictions from first-principles calculations. The contributing factors are identified and studied in detail to predict self diffusion in elemental and impurity diffusion in binary fcc/hcp-Al/Mg alloys at stable and meta-stable phases.

Finally, we investigated the role of solute segregation to the twin boundary on dynamic strain aging (DSA). Enhanced diffusivity of oxygen and subsequent segregation to the  $(10\overline{1}2)$  twin boundary in Ti poses an obstacle to further motion of the twin front; higher stresses are required to move the twin boundary, causing reduced growth under constant loading condition or "strengthening" of twinning mode. Similar to the "cross-core" diffusion process, proposed by Curtin et al. [140] in solute/dislocation interactions, strong binding energy and lower migration energy for solute segregation to the twin boundary relative to the bulk can cause DSA. DSA is a responsible microscopic mechanism for serrated yield- stress drop- in tensile loading stress-strain curves. We developed an analytical model to calculate the pinning stress that segregated O interstitials exert on twin growth. Without any fitting parameter and with the purely DFT-driven inputs, our model could predict the additional strengthening as well as strain-rate and temperature conditions for DSA as a result of solute segregation to the twin boundary. We also extended the model for substitutional solute segregation diffusing via vacancy-mediated mechanism. Using this model and DFT calculations, additional strengthening versus strain-rate at different temperatures is predicted for Mg-Al and Mg-Gd alloys. Our findings present a new mechanism for dynamic strain aging as a result of interstitial and substitutional solutes segregation to the twin boundaries.

In summary, the results presented in this work shed light on the importance of twinning in plastic deformation of hcp alloys and studies how the addition of solutes affect the nucleation and growth mechanisms. Specifically, alloying offers an effective, practical and affordable approach to tailor the mechanical properties. Proposed computational framework can be used to predict the effect of different alloying elements in various symmetrical grain (and twin) boundaries in hcp materials from the finest scale atomistic simulations.

#### 8.2 Limitations and Future Directions

Though the approach illustrated in this dissertation can be applicable to study any given symmetrical boundary or solute without losing the generality, there remain some concerns and needed to be addressed. It is important to note that solute diffusivities reported in this study are evaluated in "dilute" limit. Dilute assumption is necessary for the predictions from two important sides: (1) the Green function method developed for calculating the diffusivities from first-principles inputs evaluates the Onsager transport coefficients in a dilute alloy where the interactions between several defects i.e. vacancies or solutes are neglected, and (2) assessing the dilute limit in DFT calculations requires comparatively larger cell sizes were solute atoms would not interact with their periodic images.

The models developed in Chapter 6 and Chapter 7 provide physical justification about the conditions necessary for occurrence of DSA resulting from the solute/twin boundary interactions. However, DSA phenomenologically can occur due to other segregation events including dislocation impediment by solutes or even solute binding to the stacking faults. To be able to rigorously predict the DSA in polycrystalline materials where various deformation modes and defects are present simultaneously, a physical model requires to take the collective effects of various solute/defects segregations into the account. Therefore, the application of proposed model would be limited to the cases where the only active deformation mode is twinning. However, an advantage would be the ability to predict strain-rate dependent strengthening purely from DFT inputs and without the use of any fitting parameter. In addition, one simplified assumption in DSA prediction of substitutional solutes is using the DFT evaluated diffusivities in bulk rather than near the boundary diffusivity to assess waiting time, while it is expected that solute diffusivities to be different near the twin boundary. This in fact affects the strain-rate regime that DSA is expected to occur at a given temperature. Therefore, accurate prediction of vacancy-mediated diffusivity, similar to the diffusion model developed in Chapter 4 for interstitial case, can rectify the prediction of DSA onset in substitutional solute and twin boundary interaction model.

In dislocation/grain boundary interaction simulations, it is useful to consider the temperature effects on the generated defects using MD simulations. Also, NEB calculations can be performed to quantify the mobility of nucleated defects at the elevated temperatures. Additionally, performing similar interaction studies in the alloys with presence of other solutes would be interesting where solutes can interact and generate additional defects. While there is lack of accurate empirical potentials for different solutes in Ti and direct DFT calculations may not be practically feasible to study the dislocation / random grain boundaries, alternative techniques can be employed. With recent progress in developing new machine learning (ML) algorithms, one efficient direction would be incorporating ML-based interatomic potentials extracted from DFT calculated material properties. High-throughput DFT calculations can also be performed on symmetrical and near coincident lattice (CSL) boundaries in presence of solutes to generate generic datasets. Using advanced ML algorithms, models can be developed and trained on accurate DFT datasets and then be used to perform dislocation / grain boundary simulations. Artificial neural network is a powerful algorithm that generalizes well and is less prone to overfitting, however it requires large datasets for training. Depending on the desired properties and due to the limited number of available elements, it might not be feasible to gather large enough dataset through DFT. Therefore, implementing more advanced algorithms such as ensemble learning or recently developed Bayesian probabilistic models can be a great asset in potential development and materials discovery. The advantage of proposed method is to achieve close to DFT accuracy in prediction of desired properties but in the MD level length/time scale.

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