ATOMISTIC SIMULATIONS OF DEFORMATION MECHANISMS IN ULTRA-LIGHT WEIGHT Mg-Li ALLOYS

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Mg alloys have spurred a renewed academic and industrial interest because of their ultra-light-weight and high specific strength properties. Hexagonal close packed Mg has low deformability and a high plastic anisotropy between basal and non-basal slip systems at room temperature. Alloying with Li and other elements is believed to counter this deficiency by activating non-basal slip by reducing their nucleation stress. In this work I study how Li addition affects deformation mechanisms in Mg using atomistic simulations.

In the first part, I create a reliable and transferable concentration dependent embedded atom method (CD-EAM) potential for my molecular dynamics study of deformation. This potential describes the Mg-Li phase diagram, which accurately describes the phase stability as a function of Li concentration and temperature. Also, it reproduces the heat of mixing, lattice parameters, and bulk moduli of the alloy as a function of Li concentration. Most importantly, our CD-EAM potential reproduces the variation of stacking fault energy for basal, prismatic, and pyramidal slip systems that influences the deformation mechanisms as a function of Li concentration. This success of CD-EAM Mg-Li potential in reproducing different properties, as compared to literature data, shows its reliability and transferability.

Next, I use this newly created potential to study the effect of Li addition on deformation mechanisms in Mg-Li nanocrystalline (NC) alloys. Mg-Li NC alloys show basal slip, pyramidal type-I slip, tension twinning, and two-compression twinning deformation modes. Li addition reduces the plastic anisotropy between basal and non-basal slip systems by modifying the energetics of Mg-Li alloys. This causes the solid solution softening. The inverse relationship between strength and ductility therefore suggests a concomitant increase in alloy ductility. A comparison of the NC results with single crystal deformation results helps to understand the qualitative and quantitative effect of Li addition in Mg on nucleation stress and fault energies of each deformation mode. The nucleation stress and fault energies of basal dislocations and compression twins in single crystal Mg-Li alloy increase while those
for pyramidal dislocations and tension twinning decrease. This variation in respective values explains the reduction in plastic anisotropy and increase in ductility for Mg-Li alloys.
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CHAPTER 1

INTRODUCTION

1.1. Motivation and Background

Modern manufacturing and technological advancements are directed towards better material performance while simultaneously minimizing the resource utilization and toxic emissions and maximising the recyclability and safety. This can be achieved by modifying the individual components of the devices. Consequently, the major part of the recent research has been devoted to developing such materials that will fulfill the stringent demands of the 21st century. Mg alloys are one such promising material system because of their ultra-light weight and high specific strength. This has spurred a renewed interest, both academically and industrially. Hexagonal close packed (hcp) Mg has a number of advantages such as low density, high specific strength and stiffness. However, the applications of the hcp Mg are hampered mainly by its low ductility and formability because of the presence of fewer than five active slip systems at room temperature [29]. Methods such as grain refinement and alloying have been proposed to overcome this deficiency. For example alloying with Li is known to activate non-basal slips and reduce the critical resolved shear stress for non-basal slip systems, which increases the ductility and formability. Furthermore, it reduces the density of Mg and is soluble up to 17 atomic % in Mg at room temperature [29]. The main aim of this dissertation is to understand the effect of Li addition on the deformation of Mg and hopefully enhance our knowledge to design better future materials. Note that in real life applications multicomponent Mg-Li-X alloys are used (where, X can be one or more of Al, Zn or Mn), I use Mg-Li as a simple experimental binary surrogate alloy to study the deformation mechanisms.

Numerous experimental studies have been performed on deformation of coarse-grained (>100 nm) Mg-Li alloys [5, 30, 6, 31, 32, 33, 34]. However, many aspects of defect processes and their effect on the strength of the hcp Mg-Li alloys at the nanoscale (<100 nm) are unclear. Nanoscale materials often have higher strength and toughness but at the cost of
lower ductility [35]. The increased strength incentive coupled with the drive to miniaturize the existing devices have lead to development of micro and nano electromechanical system (MEMS and NEMS respectively). An in-depth analysis at the nanoscale will help us to understand the atomic processes that contribute to deformation and structure-property relationship. This will lead to better design and manufacturing of the devices at the nano or micro level and bulk sizes. Therefore, in this work I present atomistic simulations results of the deformation mechanisms in nanocrystalline and single crystal hcp Mg-Li alloys.

Atomistic simulations methods such as molecular statics (MS), molecular dynamics (MD), and first principles (FP) are based on the Newton’s equations of motion or the Schrödinger equation. They can provide qualitative and quantitative insights into the deformation mechanisms at nanoscale grain sizes. Such insights are difficult to access and thoroughly analyze experimentally. Atomistic simulations methods have been successfully used in last three decades to explain different phenomena that include hall-petch and inverse hall-petch type size effects with reduction in grain size and strength and defect processes in single crystal nanoparticles [36, 37, 35, 38, 7]. However, these simulations have mostly been used to study face-centered-cubic (fcc) and body-centered-cubic (bcc) nanocrystalline materials [39, 40, 41, 42]. Fewer studies have been devoted to the hcp Mg nanocrystalline system [43, 44, 45, 46, 47, 48], and I found no atomistic study specific to the hcp Mg-Li system. Present work aims to comprehensively present the physics of atomistic deformation processes important to strength and ductility in the hcp Mg-Li system.

The first part of the thesis is dedicated to the creation of a reliable and transferable Mg-Li interatomic potential needed for the MD study of the NC Mg-Li alloys. Whereas the second part discusses the atomistic process in the deformation of NC Mg-Li alloys and single crystal Mg-Li alloys. The subsection 1.2 introduces the detailed research problem of this work followed by the discussion of contents for each chapter.

1.2. Research Hypothesis

In this section, I present the research hypotheses based on the experimental results that I will test in this dissertation.
Experimental Results

Yoshinaga et al. [5] in 1963 showed that the Li addition in pure Mg increases the ductility. They also observed that the Li addition, increases the resolved shear stress for basal dislocations and decreases for pyramidal dislocations. Based on these results, they postulated that the Li addition increases the ductility by increasing the non-basal dislocation density in the Mg-Li alloys. Later in 2000’s, Agnew et al. [6, 31, 32] showed texture simulations and transmission electron microscopy characterization methods to show that the Li addition in Mg increases the non-basal \( \langle c+a \rangle \) dislocation densities. Based on these results, I postulate the following hypotheses that I address in this thesis.

**Hypothesis 1:** The Li addition in Mg increases the ductility and also increase non-basal pyramidal dislocation density in Mg-Li alloys.

**Hypothesis 2:** The Li addition increases the ductility by reducing the plastic anisotropy between basal and non-basal slip systems. It increases the stacking fault energy (SFE) and nucleation stress for the basal slip system while decreasing in these quantities for non-basal dislocations. The respective increase and decrease in such quantities for basal and non-basal slip systems reduces the plastic anisotropy.

1.3. Research Problem

The research aims to investigate the effect of Li addition on the fundamental deformation processing in Mg. This dissertation has the following components.

1. Creating a reliable interatomic potential for MD simulations of Mg-Li alloy

Interatomic potential provides the description of interatomic forces between one or different elements under consideration and are used as an input for Molecular dynamics (MD) simulations. A reliable Mg-Li interatomic potential for MD simulations was not available previously. Therefore, I create an interatomic potential for Mg-Li [49] based on the concentration dependent embedded atom method (CD-EAM) formalism developed by Caro et al. [9]. The transferability and reliability of this potential is discussed by calculating various properties of the Mg-Li system and validating the results with relevant literature data.
Studying the deformation mechanisms of nanocrystalline Mg-Li alloys

I use the newly created CD-EAM Mg-Li potential to study the deformation processes in nanocrystalline (NC) Mg-Li alloys with randomly oriented grains. An attempt has been made to correlate the results to the real experimental Mg-Li system. Different deformation modes contribute the deformation mechanisms in NC samples. I attempt to comprehensively analyze of the effect of the Li addition on the strength and deformation mechanisms in the NC Mg-Li alloys.

Mechanical behavior and deformation mechanisms of single crystal Mg-Li alloys

Single crystal simulations are carried out to benchmark the observed processes in NC Mg-Li alloys. They will allow us to study the Li effect on each deformation mechanism separately and understand how it affects NC deformation. Two parameter model is formulated to study the effect of Li addition in single crystals. These parameters are fault energy, stacking and twin fault energy, and nucleation stress for each deformation mode.

1.4. A roadmap for the rest of this dissertation

Chapter 2 reviews the literature. First, the properties and applications of Mg and Mg-Li alloys are reviewed, which will provide a justification for studying the Mg-Li system. Next the deformation modes in hcp crystal structure are described. And finally, the chapter reviews the experimental and simulation work on the Mg-Li alloys relevant to the present work.

The basics of atomistic simulation methods such as molecular statics, molecular dynamics, and First Principles are introduced in chapter 3. Their formalisms, underlying assumptions, applications, and limitations are discussed here.

Chapter 4 explains the CD-EAM methodology and its application to create the Mg-Li interatomic potential. The strategy and inputs used to create potential are presented. The reliability of our Mg-Li potential is validated by calculating and comparing different properties with literature data in chapter 5. These properties include lattice parameter,
heat of mixing, bulk modulus, phase diagram, and stacking fault energy variation with the Li addition.

Chapter 6 and 7 deal with the application of our CD-EAM potential to atomistic simulations of Mg-Li alloys. Uniaxial compression results of nanocrystalline Mg-Li alloys are presented in chapter 6. Specifically, the effect of the Li addition on strength, ductility, deformation modes, and formability of Mg-Li alloys is presented in this chapter. Chapter 7 deals mainly with single crystal simulations to explain the observed phenomena in the NC alloys. Single crystal properties of each deformation modes such as fault energy and nucleation stress are studied and analyzed to explain the behavior of the NC Mg-Li alloys.

In summary, the first part of the thesis focuses on creating a reliable interatomic potential for atomistic study and second part deals mainly with its applications to study deformation processes in the Mg-Li system.
CHAPTER 2

LITERATURE REVIEW

This chapter reviews the literature on the Mg, Mg-Li, and other Mg based alloys. Section 2.1 gives a brief overview of Mg technology, and section 2.2 outlines the crystallography of the hcp structure. Finally, the reviews of the work done on the Mg-Li and outlines of the unanswered questions in section 2.3.

2.1. A brief review of History, Mechanical properties and Applications of Mg alloys

2.1.1. History

![Figure 2.1. The world production of primary Mg metal [2].](image)

The future activities, developments, and applications of Mg were laid out in in 1808 when Sir Humphrey Davy discovered and isolated the metal by decomposing wet Mg sulphate by electrolysis using a voltaic cell and a mercury cathode [29, 3]. Mg was first commercially produced in the middle of the nineteenth century using the Deville-Caron process in which Magnesium chloride is reduced using potassium. Johnson Matthey & Co. in England used the same process for commercial Mg production in 1860. After the initial discovery, it took another 100 years to develop the demand of Mg alloys in daily life. After the second world
war, there was a rapid surge in the use of Mg for structural and aircraft applications. Over 228,000 tons of Mg was used in 1944, but this demand subsided because of the low ductility, high costs, and the difficulty in processing Mg. It took more than 45 years to reach the same level of usage. Since 1993, Mg based alloys have shown a renewed resurgence academically and industrially. Figure 2.1 shows the cumulative worldwide production of Mg metal. It can be seen that the amount of Mg produced is almost the same in 1944 and 1992, and there is surge in Mg usage after 1993. The weight savings advantage of Mg based alloys is the driving force for this renewed interest in automobile, sports, and household applications [3].

2.1.2. Properties of Mg and Mg based alloys

Mg, an alkaline earth metal, comprises 2.7 % of the earth’s crust and is the 8th most abundant element. It has many advantageous properties. It is the lightest structural metal with low density (1.5 and 5 times lower than Al and Steel respectively) and has high values of specific strength, stiffness, electrical conductivity, damping capacity, and heat dissipation. In addition, ease of machining, forming, and recycling makes Mg an attractive material for many applications [2]. Despite these advantages, the use of hexagonal close packed (hcp) Mg is limited mainly by the presence of only one active basal slip system at room temperature and large plastic anisotropy of nucleation between basal and non-basal slip systems [3, 2].

Alloying with other metals is known to counter these deficiencies and make Mg attractive to engineering applications. The most common alloying elements in Mg are Al, Zn, Li, Ca, Ag, Mn, Th, Y, and Zr. The other elements (Be, Cu, Ni, Fe, Sn) are added in very small amounts as a part of the manufacturing process. Al and Zn are the most common alloying additions, and they improve the strength. Mn is usually employed with other elements such as Al. Mn improves yield strength and salt water corrosion resistance. Si improves the fluidity of the molten alloys and improves the corrosion resistance. Th and Y increase the creep resistance up to 300°C and 350°C, respectively. Zr is used as an grain refining agent [3, 2].
2.1.3. Properties of Mg-Li alloys

Li, the alloying element investigated in the present work, is the only alloying element that reduces the density of Mg alloys. The Li addition increases the ductility and elastic constants but at the cost of strength. It is soluble up to 17 atomic % in Mg at room temperature. It is believed to increase the formability by activating non-basal \(c + a\) slip systems and reducing the plastic anisotropy between basal and non-basal slip systems [50, 6]. The Mg-Li based alloys are promising candidates for industrial usage if we can overcome oxidation problems during processing, low formability at room temperature, and large creep at relatively low stresses [29, 51]. The weight-saving aspect of the Mg-Li based alloys is attractive for many applications and needs to be investigated thoroughly to optimize strength, ductility, and specific strength [3].

Mg based alloys are used for automotive, aerospace, consumer, and military applications [2, 3, 52]. Here, I will present some of the applications.

2.1.4. Applications in Automobiles and Consumer Industries

![Figure 2.2](image)

**Figure 2.2.** Applications of Mg based alloys (a) AZ91 Mg alloy gearbox housing used in 1996 VW and AUDI (b) AM50 Mg alloy used in steering wheel of VW cars. (c) Die cast Mg laptop computer case [3].
The automobile industry has estimated that a reduction in vehicle mass by 10% leads to 5% reduction in fuel consumption [3, 29]. This benefit has driven the renewed interest in Mg based alloys. An alloy component has to satisfy the needs of different parts of a vehicle such as strength, corrosion resistance, high formability, and stiffness. There are other associated requirements related to safety, comfort, and cost. Satisfying these requirements will boost the usage of Mg alloys in the automobile industries. Not surprisingly, intense research over the past few years have lead to the usage of Mg alloys in automobile components such as the drive train, interior components, body, and chassis with other parts having potential implementation in short term-span [53]. The data reported by Friedrich et al. [53, 3] indicates that approximately 25 Kgs of Mg parts are already used in cars made by VW and AUDI. These parts inclue gearbox housings, cylinder head covers, steering wheel cores, pedal cluster mountings, and door inner parts. The long term goal of 130 to 180 Kg reduction in weight can be achieved by a strong collaboration between industry and academia.

Figure 2.2 shows the usage of Mg AZ91 alloy in gearbox housings of 1996 VW and AUDI cars and usage of AM50 alloy in the steering wheel of VW cars [3]. This usage resulted in the weight reduction of 20-25% compared to Al housings. In addition to these two companies, Mg parts are being increasingly used in General Motors, Ford, Toyota, Mercedes, and Jaguar [3, 52].

The consumer applications of Mg alloys in power hand tools, lawn and garden equipments, computers and computer hardwares, electronic equipments, optical equipments, and sports equipments has been a recent development. Other miscellaneous applications include lighting fixture components, cooling fans, and split-wheels for motorized wheel chairs.

2.1.5. Applications in Aerospace Industries

Mg based alloys are being used in aerospace applications since the pre-World War II era. Figure 2.3 shows B-36, commonly referred as the Magnesium Wonder of the World, the largest bomber ever built in 1940 [3]. The total weight of the bomber was 350,000 lbs. It was the largest single user of Mg with 12,200 lbs of sheet, 1500 lbs of forgings, and 660
Figure 2.3. B-36 bomber, *the Magnesium Wonder of the World*, used many Mg parts in 1940 [3].

lbs of castings for each bomber. 25% of the exterior surface of the plane was covered with Mg skin. In present times, Boeing uses Mg parts to manufacture commercial and military aircrafts. The usage of Mg alloys has reduced in aerospace applications post World War II era because of inferior corrosion and mechanical properties combined with the fear of fires [3].

2.1.6. *Miscellaneous: Metallurgical, chemical and structural applications*

In Metallurgy, Mg is mostly used as an alloying element in Al to improve strength. Nodular cast iron manufacturing uses Mg to remove sulphur and spheriodizing the graphite, which improves the ductility. In brass and bronze manufacturing, Mg is used as deoxidizer or scavenger. For chemical applications, the Grignard process uses Mg to produce complex organic and organometallic compounds. Mg is also used as sacrificial galvanic anode to extend the life of cables, pipelines, and tanks. The lightweight aspect of Mg makes it attractive for structural applications in moving parts. Low density of Mg results in low inertia, which is useful in rapidly moving parts. Low density is also useful to manufacture thick parts. Historically, Mg is extensively used for military applications such as shelter frames, mortar
bases and missiles, surface-vehicle frames, panels, and floors [29, 3]. Household items, sewing machines, and archery bows, also use Mg [29].

These different applications coupled with the growing demands of Mg based alloys indicate a need for the thorough examination.

2.2. Crystallography and Deformation modes in hexagonal close packed (hcp) metals

This section briefly reviews the crystallography and deformation modes in the hcp crystals [54, 55, 56].

2.2.1. Crystallography of the hcp crystals

For a primitive hexagonal unit cell, box vectors are $a_1 = a_2 \neq a_3$ and box angles are $\alpha = \beta = 90^0$ and $\gamma = 120^0$ as shown in figure 2.4(a). The atoms in the primitive unit cell are located at fractional coordinates $(0,0,0)$ and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$. This crystal is usually illustrated as a hexagonal prism with three primitive unit cells and has an AB type stacking of atomic layers as shown in figure 2.4(b). Miller-Bravais indices are used to describe directions $[a_1, a_2, a_3, c]$ and planes $(h,k,i,l)$ in the hcp structure. These are shown in figure 2.4(b) along with Miller-Bravais indices for directions and stacking planes.

2.2.2. Deformation modes in hcp crystals

Dislocations in the hcp crystal structure have three types of Burgers vectors $-\langle a \rangle$, $\langle c \rangle$, and $\langle c + a \rangle$ as shown in figure 2.5. These Burgers vectors are observed on different slip planes shown in figure 2.5. A slip plane together with an associated Burgers vectors constitute a slip system. $\langle a \rangle$ type of Burgers vector is most common and is observed on basal, prismatic, and pyramidal planes. $\langle c \rangle$ type vector is observed only on a prismatic plane, while $\langle c + a \rangle$ vector is observed on pyramidal type I and II, and other twinning modes.

The so called Von Mises criterion requires five independent slip systems for a homogeneous deformation of a polycrystalline material without change in volume [57]. Figure 2.6 shows that six types of slip systems and other deformation modes are theoretically available in the hcp metals. However, at room temperature basal slip is the most predominant deformation mode in metals with $\frac{c}{a} \geq 1.633$ like Mg, Zn, and Co (except Be) while prismatic slip
Figure 2.4. (a) Primitive hexagonal unit cell (b) Axes/angles and AB type stacking in a hexagonal crystal structure.

is most common in metals with $\frac{c}{a} \leq 1.633$ like Ti, Zr, and Hf. Prismatic $\langle c \rangle$ and Pyramidal $\langle c + a \rangle$ slip systems are activated mainly at high temperatures or by high stresses generated at interfacial regions.

The independent slip systems are shown in figure 2.6. Basal and prismatic slip systems, which are observed most commonly at room temperature, in hcp metals cover only four independent slip systems and cannot satisfy the Von Mises criterion because slip systems from 4 to 7 shown in figure 2.6, are not easily activated. Furthermore, type 1, 2, and 3 shown in figure 2.6 act along $\langle a \rangle$ direction and cannot produce deformation along $\langle c \rangle$. Thus, homogeneous deformations in the hcp metals cannot be attributed to $\langle a \rangle$ type slip. Therefore, twinning systems from 8 to 10 in figure 2.6 and shown schematically in figure 2.5 provide additional deformation modes in the hcp systems and play an important role in deformations [45, 56]. $\{10\overline{1}2\} \langle 10\overline{1}1 \rangle$ tensile twinning (TTW) with 86.3$^0$ angle, $\{10\overline{1}1\} \langle 10\overline{1}2 \rangle$ compressive twinning (CTW1) with 56$^0$ angle, and $\{10\overline{1}3\} \langle 3032 \rangle$ compressive twinning (CTW2) with 64$^0$ angle are the most commonly observed twinning modes in hcp Mg and its alloys. The
Figure 2.5. Figure shows the slip plane and associated Burgers vectors for different slip systems. (a) Basal plane \{0001\} \langle11\bar{2}0\rangle, Prismatic plane \{10\bar{1}0\} \langle11\bar{2}0\rangle, Pyramidal plane type I \{10\bar{1}1\} \langle11\bar{2}3\rangle, and type II \{11\bar{2}2\} \langle11\bar{2}3\rangle slip systems (b) tension twinning (TTW) \{10\bar{1}2\} \langle10\bar{1}1\rangle, compression twinning (CTW1) \{10\bar{1}3\} \langle30\bar{3}2\rangle, and compression twinning (CTW2) \{10\bar{1}1\} \langle10\bar{1}2\rangle.

<table>
<thead>
<tr>
<th>No.</th>
<th>Deformation Mode</th>
<th>Burgers vector</th>
<th>Slip direction</th>
<th>No. of slip systems</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Total</td>
</tr>
<tr>
<td>1</td>
<td>Basal {0001}</td>
<td>\langle a \rangle</td>
<td>\langle 10\bar{1}0 \rangle</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>Prismatic {11\bar{1}0}</td>
<td>\langle a \rangle</td>
<td>\langle 11\bar{2}0 \rangle</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>Pyramidal slip {11\bar{1}1}</td>
<td>\langle a \rangle</td>
<td>\langle 11\bar{2}0 \rangle</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>Prismatic-I {11\bar{1}0}</td>
<td>\langle c \rangle</td>
<td>\langle 0001 \rangle</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>Prismatic-II {11\bar{2}0}</td>
<td>\langle c \rangle</td>
<td>\langle 0001 \rangle</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>Pyramidal type I {10\bar{1}1}</td>
<td>\langle c+a \rangle</td>
<td>\langle 11\bar{2}3 \rangle</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>Pyramidal type II {11\bar{2}2}</td>
<td>\langle c+a \rangle</td>
<td>\langle 11\bar{2}3 \rangle</td>
<td>6</td>
</tr>
<tr>
<td>8</td>
<td>Tensile twin {10\bar{1}2}</td>
<td></td>
<td>\langle 10\bar{1}1 \rangle</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Compressive twin {10\bar{1}1}</td>
<td></td>
<td>\langle 1\bar{1}02 \rangle</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Compressive twin {10\bar{1}3}</td>
<td></td>
<td>\langle 30\bar{3}2 \rangle</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.6. Deformation modes in hcp metals are summarized here.
angle for these twinning planes is calculated as the angle between the equivalent planes in a Mg hcp unit cell. Other twinning modes such as \{112\1\} \langle \overline{1}126 \rangle have also been reported [58, 59].

\[\text{Figure 2.7.} \text{ Schematic representation of the angle calculation for the twin systems. The angle is calculated between the two equivalent planes in a hcp unit cell. Refer text and previous figures for TTW, CTW1, and CTW2 description. (a) 86.3° angle for TTW (b) 56° angle for CTW1 and (c) 64° angle between two equivalent CTW2 planes.}\]
2.3. Previous work on Mg-Li alloys

2.3.1. Thermodynamics of Mg-Li alloys

Grube et al. [60] first studied the Mg-Li phase diagram studies in 1934. Since then, numerous authors have attempted to demarcate the correct phase boundaries for the Mg-Li system at different temperatures [61, 62, 63, 4]. The Mg-Li phase boundaries determined by Hansen et al. [61] experimentally are widely accepted now. Figure 2.8 shows the Mg-Li phase diagram re-drawn from Saunders in 1990 [4]. The general characteristics of Mg-Li phase diagram consists of a liquid phase, Mg solid solution (\(\alpha\)) with 17 atomic% Li solubility, Li solid solution (\(\beta\)) with 70 atomic% Mg solubility, a two phase (\(\alpha + \beta\)) region from 17 to 30 atomic% Li solubility and a eutectic point near 23 atomic% Li, and 861 K temperature. \(\alpha\) and \(\beta\) phases have the hcp and bcc crystal structures, respectively.

I have reproduced this phase diagram using MD for the Mg-Li system and this will be discussed in detail in the coming chapters. This is the first Atomistic simulations calculations of a phase diagram for this system.

![Mg-Li phase diagram](image)

**Figure 2.8.** Mg-Li phase diagram [4]
2.3.2. Deformation properties of Mg-Li alloys

This subsection presents the results of previous experimental and simulations studies related to the thesis. The studies by Yoshinaga et al. and Ahmadieh et al. form the background for the recent research on Mg-Li alloys [5, 30].

Yoshinaga et al. found that the Mg-Li alloys showed considerably higher ductility than pure Mg. They also observed that the flow stress of polycrystalline samples decrease with increasing Li content (when, >0.4 At % Li). The resolved shear stress increases for basal slip and decreases for non-basal slips (prismatic and pyramidal) with the Li addition at room temperature. Based on these results, they concluded that non-basal slip might be inactive in pure Mg and might occur readily in the Mg-Li alloys leading to their increased ductility. Ahmadieh et al. also found that the Li addition decreases critical resolved shear stress for prismatic slip. Figure 2.9 shows the critical resolved shear stress obtained by Yoshinaga et al. for basal and non-basal slip systems. Both these studies did not conclusively prove that the Li addition increases ductility by activating non-basal slip because of the experimental limitations in early 1960s.

![Figure 2.9](image)

**Figure 2.9.** Critical resolved shear stress for (a) basal and (b) prismatic slip [5].
The increase in ductility and a suggestion that non-basal slips might be active in Mg-Li alloys motivated the researchers to look closely at the Mg-Li alloys. More recently, Agnew et al. [6, 31, 32] used texture simulations and transmission electron microscopy to study the Mg-Li system. The advanced experimental, characterization, and simulation techniques showed that addition of Li decreases flow stress and basal activity, increases non-basal \((c + a)\) activity, and distributes non-basal \((c + a)\) dislocations uniformly in the sample [6, 31, 32]. Figure 2.10 shows such an example by Agnew et al. [6] where non-basal activity is substantially present. More recently, Lentz et al. [34] experimentally showed the presence of tension twinning and compression twinning deformation modes in micrometer sized samples.

![Figure 2.10](image.png)

**Figure 2.10.** The relative fraction or activity of each deformation mode in the Mg-3%Li alloy by texture simulations [6].

Atomistic simulations studies on the Mg-Li system are scarce. Han et al. and Muzyk et al. showed that the stacking fault energies in Mg-Li [19, 20] increase with Li addition. Kim et al. and Karewar et al. have created the interatomic potentials for large scale simulation studies of deformation mechanisms such as done in present thesis [17, 49]. Yasi et al., Moitra et al. and Han et al. studied the solute effects of Li in Mg [64, 65, 19].
The experimental studies are carried out above nanoscale sizes (>100nm) and an in-depth analysis by Atomistic simulation methods is still lacking in the literature. The present thesis aims to address both these issues and tries to enhance the knowledge about deformation of the Mg-Li alloys.

2.3.3. Interatomic potential for Mg-Li alloys

A reliable interatomic potential for the large scale simulation was not available earlier. Pseudo-potentials [27, 66] were mainly created in 1975 and 1996, respectively, to study the bcc and liquid phase, respectively, and the modern large-scale simulations are still beyond the capabilities of these potentials. Second nearest neighbor modified embedded atom method potential (2NN MEAM) for Mg-Li [17] was developed only recently. This potential appears to provide a good description of different properties. Although, the stacking fault energy (SFE) trends for MEAM Mg-Li potential do not match with literature and authors of this potential do not validate the phase stability as a function of temperature. Therefore, I aim to create a reliable and transferable interatomic potential for the Mg-Li binary alloy, which will be useful to study the deformation mechanisms at finite temperatures. The new Mg-Li potential will be based on the robust concentration dependent embedded atom method (CD-EAM) model, which is successfully used to describe different alloy systems [10, 9, 67, 68, 69, 70, 71, 72, 73].

2.4. Summary

Applications of Mg based alloys in automotive, aerospace, and consumer sectors, increasing production, and demand of Mg based alloys driven by the weight saving advantage motivates this study. The present atomistic simulations study aims to understand the interesting effects of the Li addition in Mg such as increase in ductility, decrease in basal activity, and increase of non-basal activity. Previous experimental studies were done above nanoscale sizes (>100nm) and atomistic input on deformation mechanisms in Mg-Li alloys is still lacking. Furthermore, a reliable interatomic potential for large scale atomistic simulations was not available. This work aims to address these issues.
CHAPTER 3

ATOMISTIC SIMULATION METHODOLOGY

3.1. Introduction

Multiscale modeling methods have been used to study the fundamental science phenomena in last few decades over multiple spatial and temporal scale windows. Different multiscale modeling methods are shown in the figure 3.1 and elaborated in many publications [74, 75, 8, 38]. Atomistic simulations are used at nano length and time scales and consists of first principles (Quantum Mechanics), molecular dynamics (MD), and monte carlo (MC) methodologies. I am mainly using MD and MS techniques in my research and will briefly describe these methods below. In atomistic simulations, atoms are represented as point mass and an interatomic potential describes their potential energy as a function of interatomic distance. MS uses numerical optimization algorithms to minimize the potential energy of the system at 0K. Whereas MD is carried out at a finite temperature by updating atom positions and velocities as a function of time. I also used DFT (Density Functional Theory) method to solve the Schrödinger equation and calculate material properties like lattice constants, elastic moduli, stacking fault energies, and other crystal defect energies discussed in the next chapter.

3.2. Density Functional theory (DFT) calculations

Now I briefly describe the DFT methodology that I used to calculate the stacking fault energy of basal and prismatic planes in chapter 5. DFT is a type of first principles or \textit{ab initio} methodology that is highly transferable but limited to few hundreds of atoms because the calculations are computationally expensive. A more extensive description of this methodology can be found in references [77, 78, 79].

The DFT method solves the non-relativistic time independent Schrödinger’s equation with Hamiltonian $H$, wave function $\Psi$, and energy of the particular state $E$ given by,
Figure 3.1. Multiscale modeling methods across different length and time scales. The coupling between different modeling methods is shown in the overlapped regions. [74, 75]

\[ H\Psi(r) = E\Psi(r) \]

This Hamiltonian is simplified using the Born-Oppenheimer (BO) approximation. BO approximation assumes that the motion of a heavier mass nucleus can be ignored compared to electrons. Thus, electrons are assumed to adjust instantaneously to the new nucleus position. Under the BO approximation in the Schrödinger’s equation, Hamiltonian is written as,

\[ -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_i V_{\text{ext}}(r_i) + \sum_{i\neq j} U(r_i, r_j) \] \[ \Psi(r_1, r_2, ..., r_N) = E\Psi(r_1, r_2, ..., r_N) \]
Here first, second, and third terms on the left side are kinetic energy of electrons, external potential acting on electrons from nuclei, and electron-electron interactions respectively.

The goal is to solve the equations 1 and 2 to find the ground-state minimum energy $E_0$. Unfortunately the solution based on the wave function approach is unsuitable for large solids with many interacting atoms because the solutions of the Schrödinger’s equation increase exponentially with number of electrons. Thus, some simplifying assumptions need to be made as described next.

For DFT, Hohenberg and Kohn [80] and Kohn and Sham [81] simplified the Schrödinger’s equation by replacing the many-body electron wave functions with electron density to calculate the total energy. In DFT, the total energy of an atomic system can formulated as,

\begin{equation}
E = E[\rho]
\end{equation}

Where $\rho = \rho(r)$ is a scalar electron density function defined at each point, $r$, in real space.

Kohn and Sham replaced the real electrons of an atomic system by non-interacting effective electrons with the same charge, mass, and density distribution in an effective potential. The total energy of the system in equation 3 is given as,

\begin{equation}
E = T_0 + U + E_{xc}
\end{equation}

Here $T_0$ is the kinetic energy of the electrons, and $U$ is total Coulomb energy consisting of the interaction between electrons-electrons, electron-nuclei, and nuclei-nuclei. The last term in equation 4, $E_{xc}$, is the exchange-correlation energy term. It consists of two terms, namely exchange energy and correlation energy. Exchange energy is the reduction in Coulomb’s repulsion energy as per the Pauli’s exclusion principle when an electron with a given spin avoids all other electrons with the same spin. Whereas correlation energy is related to the many body interaction terms between electrons of opposite spin.
The exact many body electron density is given as,

\begin{equation}
\rho(r) = \sum_i n_i |\Psi_i(r)|^2
\end{equation}

Now using the Kohn-Sham effective potential, the Schrödinger’s Hamiltonian in DFT is rewritten as the so-called Kohn-Sham equations,

\begin{equation}
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(r) \right] \Psi_i(r) = \epsilon_i \Psi_i(r)
\end{equation}

Where $V_{\text{eff}}(r) = V_c(r) + \mu_{\text{xc}}[\rho(r)]$. The electron density $\rho$ is the ground state density corresponding to the wave function that minimizes the total energy. $\epsilon_i$ is the effective one electron eigenvalues termed as Lagrange multipliers.

The Hamiltonian in equation 6 contains three terms. The first term is the kinetic energy term whose construction does not require specific knowledge of the system. Whereas the Coulomb potential operator $V_c(r)$ and the exchange-correlation operator $\mu_{\text{xc}}$ need electron density of the system under consideration and are given as,

\begin{equation}
V_c(r) = -e^2 \sum_\alpha \frac{Z_\alpha}{|r - R_\alpha|} + e^2 \int \frac{\rho(r')}{|r - r'|} dr'
\end{equation}

and

\begin{equation}
\mu_{\text{xc}} = \frac{\partial E_{\text{xc}}[\rho]}{d\rho}
\end{equation}

Here, $R$ and $r$ represents the positions of the ions and electrons, respectively.

The exchange-correlation energy $E_{\text{xc}}$ can be calculated using Local Density Approximation (LDA) that approximates the $E_{\text{xc}}$ from the local electron density around each volume element $dr$ as,

\begin{equation}
E_{\text{xc}}[\rho] = \int \rho(r) \epsilon_{\text{xc}}^0[\rho(r)] dr
\end{equation}
LDA takes into account only the local electron density and the predicted properties, such as bond lengths and binding energies, vary considerably compared to experimentally measured values. To counter this, the generalized gradient approximation (GGA) \cite{82} takes into account the non-local exchange-correlation effects and considers the exchange-correlation functional as a function of gradient of electron density. The GGA corrections are also referred as non-local potentials. The properties predicted by GGA compare well with the corresponding experimentally determined values.

The energy within GGA approximation is written as,

\begin{equation}
E_{GGA} = E_{LSD} + E_{G}^{X} + E_{G}^{C}
\end{equation}

Where $E_{LSD}$ is the local spin density approximation given by Barth et al. \cite{83} and Gunnarson et al. \cite{84}. Gradient corrected exchange $E_{G}^{X}$ and gradient corrected correlation $E_{G}^{C}$ are given by Becke \cite{85} and Perdew \cite{86}, respectively, as,

\begin{equation}
E_{G}^{X} = b \sum \int \frac{\rho_{\sigma}x_{\sigma}^{2}}{1 + 6b_{x_{\sigma}} sinh^{-1}(x_{\sigma})} dr
\end{equation}

(11)

\begin{equation}
E_{G}^{C} = \int f(\rho \downarrow, \rho \uparrow) e^{-g(\rho)|\nabla \rho|^2} |\nabla \rho|^2 dr
\end{equation}

(12)

Where $x_{\sigma} = |\nabla \rho|/e^{3}$ and $\sigma = \uparrow$ or $\sigma = \downarrow$. In Becke’s formula, $b$ is fitted to the exchange energy of inert gases.

The last thing is the formulation of the plane wave basis set to solve these equations. Using Bloch’s theorem \cite{87}, the wave function of an electron can be expressed as a product of a planewave and function of periodicity of the lattice shown in equation 13.

\begin{equation}
\psi_{nk}(r) = e^{(i\vec{k},\vec{r})} u_{nk}(\vec{r})
\end{equation}

(13)

Here $\vec{r}$ and $\vec{k}$ are the position vector and wave-vector.
The wave-function can be expressed as the expansion of periodic function \( u_{nk}(r) \) in terms of wave vectors of the reciprocal lattice, \( G \).

\[
\psi_i(r) = \sum_G c_{i,k+G} e^{i(k+G) \cdot r}
\]

Here \( c_{i,k+G} \) are the coefficients used to obtain the minimum energy solution. The plane wave basis set energy is truncated above a cutoff energy.

Finally, the atomic interactions are given by the pseudopotentials (norm-conserving soft pseudopotentials or Vanderbilt ultrasoft pseudopotentials) [88, 89]. Psuedopotentials are based on the idea that the core electrons contribute negligibly to bonding compared to valence electrons, and we can thus replace the core electrons atomic potential by an equivalent pseudopotential that has the same effect on valence electrons.

The limitations of the DFT methodology include the small simulation system size because of its computational expense. In addition, DFT needs the use of periodic boundary conditions, whereas free boundary conditions are used to describe long range fields of isolated dislocations.

3.3. Molecular Statics (MS) at T=0

The general steps followed for MS are same as MD described in section 3.4 from 1 to 5. The difference being conjugate-gradient, steepest-decent, or other algorithms are used to minimize the energy of the system instead of iterating over time as done in MD. The detailed description of these algorithms can be found in [7, 76]. MS can be used to calculate the equilibrium structure and energy at 0K. It is also useful to calculate the barriers of transformations and defects energies such as vacancy formation, migration energy, and interstitial or substitutional energies.

3.4. Molecular dynamics (MD) at T>0

MD simulations solve Newton’s equation of motion using the definition of atomic interaction. They can provide qualitatively and quantitatively insights into the deformation mechanisms at length scales that are often difficult to access experimentally. MD simulation
methodology follows the atomic trajectories of a system of particles by numerical integration of Newton’s equation of motion using interatomic potential, initial conditions, and boundary conditions. MD can be either equilibrium molecular dynamics (EMD) or non-equilibrium molecular dynamics (NEMD). EMD has fixed number of atoms (N), volume (V), and constant total energy (E) and is completely isolated from surroundings. This corresponds to microcanonical ensemble (NVE). Whereas NEMD can have constant temperature (T) or constant pressure (P) instead of energy and correspond to canonical ensemble (NVT) or constant pressure isothermal isobaric (NPT). These ensembles are discussed later in this section. Major MD steps are as follows,

1. Define initial conditions such as atomic positions, velocities, and boundary conditions.
2. Define interatomic potential and calculate forces between atoms.
3. Solve Newton’s equations of motion numerically, and update the position and velocity of each atom.
4. Use appropriate thermodynamic ensembles to perform the desired simulations. These ensembles can be NVE, NVT, and NPT.
5. Calculate the desired thermodynamic and mechanical properties, and identify crystal structure, and analyze local defects from the simulation run.

I will describe these steps in this section. Figure 3.2 shows the flow chart of the steps followed for MD simulations.

3.4.1. Define Initial conditions

Initial Atomic positions and velocities.

The initial atomic positions in 3D lattice unit at \( t = 0 \) are given as \( x^{3N}(t = 0) \) and the corresponding velocities are given as \( \dot{x}^{3N}(t = 0) \). Here, \( 3N \) corresponds to three spatial degrees of freedom. For crystalline solids, as in the present study, the \( x^{3N}(t = 0) \) is obtained from a desired lattice structure (for example, cubic and hexagonal) and the corresponding lattice constant. For liquids, the initial positions can be obtained by melting the crystalline
solid. A MD supercell is constructed by repeating the desired number of primitive unit cells along the X, Y, and Z directions.

The initial velocities of the atoms are set corresponding to the simulation system temperature according to the Maxwell-Boltzmann statistics and using equation 15. This method scales the velocities of the atoms to the corresponding temperature of interest. The other method to modify the velocities based on the canonical ensemble (NVT) is described in subsection 3.4.4.

\[
\langle \frac{1}{2} m v^2 \rangle = \frac{k_B T}{2}
\]

Here, \( m \) is mass, \( k_B \) is the Boltzmann constant, and \( v \) is the velocity of the atoms corresponding to temperature \( T \).
Initial Boundary conditions.

Figure 3.3. Illustration of the PBC in 2D [7, 8]. Primary unit cell is shown in the red shaded area. The cells surrounding the primary cell are periodic images. The atoms in the primary cell can interact with the atoms in the surrounding cells.

There are two types of boundary conditions: periodic boundary condition (PBC) and free or non-periodic boundary conditions (FPB). A simulation system can have both boundary conditions along the X, Y, and Z direction. Figure 3.3 illustrates the PBC in a 2D system [8]. Here, the central simulation cell is surrounded by its replicas called the periodic images. The atoms across the periodic images can interact. If atoms move out of the simulation cell from one side of the simulation box they can re-enter the box from other
side. PBC’s are well suited to study bulk solids and liquids. For FBC, atoms on the surface are surrounded by a vacuum and no interactions occur across the supercell boundary. FBC are suited to study systems with surface effects.

3.4.2. Interatomic potential and force calculation

In MD, the interatomic potentials describe atomic interactions to calculate forces at each iteration cycle of the simulation. The internal energy of material systems is given as a function of atomic separation. Energy of the metallic systems is most commonly described by the Embedded Atom Method (EAM), and other equivalent methods derived from density-functional theory [90, 91, 92], second-moment tight-binding [93] formalisms, and/or from experimentally derived properties. I use EAM formalism in this work.

The energy of a metal in EAM formalism is expressed as,

$$ E = \frac{1}{2} \sum_{i,j(i\neq j)} V_{ij}(r_{ij}) + \sum_i F_i \left( \sum_{i\neq j} \rho_i(r_{ij}) \right) $$

Where $V$ is a two-body term describing the energy of the pair interaction in the system at sites $i$ and $j$. $F$ captures the many-body interaction and is the energy required to embed an atom $i$ in the local electron density provided by the remaining atoms of the system. $\rho$ is the spherically or non-spherically averaged atomic electron density and is calculated for each atom by evaluating superposition of atomic density from its neighbors.

EAM takes into account many body effects in metallic bonding to calculate the cohesive energy and has better predictability than Lennard-Jones (LJ) pair potentials for metals. The inventions of EAM potential enabled the simulations of multimillion atom systems of metals and alloys. EAM has been successfully applied to many bulk and interface problems involving mechanical and thermodynamic properties of solids and liquids, phonon calculations, grain boundary structures and segregations, and fracture [92].
Once the interatomic interaction is defined, we can calculate the forces acting on atoms as,

\begin{equation}
\vec{F}_i = -\vec{\nabla}\Phi
\end{equation}

Where \( i = 1, 2, 3, ..., N \), \( \vec{\nabla} = \hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z} \), and \( \Phi \) is the energy.

3.4.3. Numerical integrators to update positions and velocities

The Velocity Verlet algorithm [94] is one of the most commonly used time integration schemes in MD simulations. It consists of two Taylor expansions for positions \( \vec{r}(t) \), one forward, and one backward in time as follows,

\begin{equation}
\vec{r}(t - \Delta t) = \vec{r}(t) - \vec{v}(t)\Delta t + \frac{1}{2}\vec{a}(t)\Delta t^2 - \frac{1}{6}\vec{b}(t)\Delta t^3 + ...
\end{equation}

\begin{equation}
\vec{r}(t + \Delta t) = \vec{r}(t) + \vec{v}(t)\Delta t + \frac{1}{2}\vec{a}(t)\Delta t^2 + \frac{1}{6}\vec{b}(t)\Delta t^3 + ...
\end{equation}

Where \( \vec{V}, \vec{a}, \) and \( \vec{b} \) are the first, second, and third order derivatives of position vector \( \vec{r} \), respectively.

Equations 18 and 19 are added to get the final Velocity Verlet algorithm as,

\begin{equation}
\vec{r}(t + \Delta t) \simeq 2\vec{r}(t) - \vec{r}(t - \Delta t) + \vec{a}(t)\Delta t^2
\end{equation}

The velocity can be computed from positions as follows,

\begin{equation}
\vec{v}(t) = \frac{\vec{r}(t + \Delta t) - \vec{r}(t - \Delta t)}{2\Delta t}
\end{equation}

3.4.4. Thermodynamic ensembles (NVE, NVT, NPT)

Thermodynamic ensembles provide us the mathematical framework to study the evolution of materials. The assumption used is that the time averages are equivalent to the
ensemble averages. I used the Microcanonical (NVE), Canonical (NVT), and Isothermal-Isobaric (NPT) ensembles in the present MD study. These ensembles are described briefly in this subsection.

3.4.5. **Microcanonical ensemble (NVE)**

The number of atoms (N), volume (V), and internal energy (E) of the system are kept constant in the NVE ensemble. This ensemble represents an isolated system. The extensive property entropy S can be defined in a NVE ensemble as,

\begin{equation}
S = k_B \ln(W(N,V,E))
\end{equation}

Where \( W \) is the total number of microstates.

From this definition of the entropy, other properties such as temperature (T), pressure (P), and chemical potential (\( \mu \)) can be derived as follows:

\begin{equation}
\frac{\partial S}{\partial E} = \frac{1}{T}
\end{equation}

\begin{equation}
\frac{\partial S}{\partial E} = -\frac{P}{T}
\end{equation}

\begin{equation}
\frac{\partial S}{\partial N} = \frac{\mu}{T}
\end{equation}

3.4.6. **Canonical ensemble (NVT) and Nosè-Hoover thermostat**

In many experiments, temperature (T) of the system is kept constant and the NVE ensemble is not useful to describe such systems. Canonical ensemble (NVT) is used instead to keep the T, N, and V constant. MD simulations employing the NVT ensemble most commonly use the Nosè-Hoover thermostat [95, 96, 97, 97] to keep the temperature fixed at an average desired value.

H. C. Andersen developed a thermostat for MD simulations in 1980 [98]. In this approach, constant temperature is achieved by the stochastic collisions with the heat bath. Nosè
[95, 96] proposed an extended Lagrangian in 1984 that contains additional artificial coordinates and velocities. Later, in 1985 Hoover [97, 99] proposed another extended-Lagrangian, now called the Nosè-Hoover thermostat, that is commonly used in MD simulations.

The Hamiltonian in the Nosè-Hoover thermostat is written as,

\[
H_{\text{Nose}} = \sum_{i=1}^{N} \frac{P_i^2}{2m_i s^2} + U(r^N) + \frac{P_s^2}{2Q} + F k_B T \ln(s)
\]

Where \(r\) and \(P\) represent the coordinates and momenta of all atoms in the system, \(m_i\) is the atomic mass, \(Q\) is a fictitious mass, \(F\) is the total number of degree of freedom of the system, and \(s\) is the scaled coordinates in terms of virtual variables.

Other popular thermostats include those from Berendsen [100], Langevin [101], and explicit rescaling of velocity. Here, I describe velocity rescaling method used in present MD simulations.

The velocity rescaling method also known as Gaussian thermostat [102], is the first method proposed to keep the temperature fixed. The equipartition theorem [8, 103] gives the instantaneous temperature of monoatomic system as,

\[
\langle T_{\text{ins}} \rangle = \frac{2}{3k_B F} \sum_{i=1}^{N} \frac{1}{2} m v^2
\]

This instantaneous temperature \(T_{\text{ins}}\) is then compared with target temperature \((T_0)\) to adjust the temperature by explicitly rescaling the velocities as,

\[
v_{\text{new}} = v_{\text{old}} \sqrt{\frac{T_0}{T_{\text{ins}}}}
\]

Where \(v_{\text{new}}\) and \(v_{\text{old}}\) are the rescaled velocity and original velocity, respectively.
3.4.7. Isothermal-Isobaric ensemble (NPT)

The NPT ensemble corresponds to a simulation system that holds temperature and pressure fixed. This ensemble is most useful to replicate an experimental setup with controlled pressure and temperature variables.

Along with NVT ensemble, Andersen first introduced the pressure control in MD simulations in 1980 [98]. The drawback of this implementation is the use of hydrostatic pressure with constant cell shape. Parrinello and Rahman [104] introduced a general constant-pressure implementation to allow the variation of the simulation cell shape and size. The implementation modifies the pressure to the desired value and simultaneously accounts the anisotropic behavior of the materials. The Hamiltonian in this case is given as,

\[
H = \frac{1}{2} \sum_{i=1}^{N} m_i \dot{q}_i G \dot{q}_i - \sum_{i=1}^{N} \sum_{j>i}^{N} \Psi(|q_{ij}|) + \frac{1}{2} M_W Tr(\dot{\psi}^T \dot{\psi}) - \Omega p_o
\]

Where \(m_i\) is the atomic mass, \(q_i\) is the rescaled atomic coordinates with volume changes, \(G = \psi^T \psi\), \(\psi\) is the matrix formed by vectors of the simulation cell, \(Tr\) is the trace of the matrix, \(T\) is the transpose of the matrix, \(\Psi\) is the potential energy, \(M_W\) is the effective mass of the cell wall, \(p_o\) is the external pressure, and \(\Omega\) is the volume of the simulation system.

3.5. Calculation of the Properties

Different properties can be calculated from atomistic simulations. These include structural properties (radial distribution function), equation of state (free energy, phase diagram, thermal expansion coefficient), transport properties, plastic deformation response, and others. These properties can then be compared with literature values for accuracy that finally depends on the reliability of the interatomic potential description. Free energy calculations, phase diagram creation, heat of mixing, bulk modulus, and stacking fault energy calculations are discussed in chapter 4.
I now describe stress calculation. Virial stress [105] and Hardy stress [106] are the two most commonly used definitions for stress. Here, I will describe Virial stress calculation methods used in the present work.

Atomic virial stress $\Pi^i$ on atom $i$ is defined as,

\begin{equation}
\Pi^i = \frac{1}{\Omega^i} \left[ \frac{1}{2} \sum_i \sum_{i \neq j} \frac{U'}{r_{ij}} \alpha \beta r_{ij} - \sum_i m v_i v^i \right]
\end{equation}

Where $\Omega^i$ is the atomic volume, $r_{ij}$ is the distance between atoms $i$ and $j$, $\alpha$ and $\beta$ are the different direction indices, $U'$ is the derivative of the potential energy with respect to distance, and $v^i$ is the velocity of the atoms.

The atomic stress is averaged over the volume of the simulation cell to get the total stress tensor as,

\begin{equation}
\sigma = \frac{1}{N} \sum_{i=1}^{N} \Pi^i
\end{equation}

Where $N$ is the total number of atoms in the system.

3.6. Identification of the Local Atomic Environment using Common neighbor analysis (CNA) code

Different methods are used to characterize the local structure of the simulation system. These include centro-symmetry analysis [107], slip vector analysis [108] and common neighbor analysis (CNA) [109]. Atoms in the simulation system are sometimes also distinguished based on the atom energy. Here, I will describe the CNA method that is most commonly used method.

CNA was proposed by Honeycutt and Anderson in 1987 [109]. It is based on the four indices $l, m, n, o$ and nearest neighbor pair $i$ and $j$. For each nearest neighbor pair $i - j$ we identify these four indices as,

$m : m$ indicates the common neighbors shared by $i$ and $j$ pair. 4 for fcc structure, see figure 3.4(b).
Figure 3.4. Signatures of the local environments identified in the CNA (Common Neighbor Analysis) for fcc structure [1] with 12 nearest neighbors (NN). (a) Starting configuration for fcc crystal structure with 12 NNs for central green i atom surrounded by 12 (green and brown) atoms. Pair of nearest neighbor atoms is indicated by green atoms i and j. All other green atoms are the common neighbors of the i-j pair and brown atoms are the other atoms in the fcc structure but not shared neighbors of i-j pair. (b) 421 structure with pair i-j and its common neighbors from isolated fcc structure. The three indices 4, 2, and 1 represent the fcc structure in Atomistic simulations. Refer text for the description of these indices.

\[ n : \] \( n \) is the number of bonds between common neighbors. 2 for fcc structure, see figure 3.4(b).

\[ o : \] \( o \) indicates the number of bonds in the longest bond formed by the shared neighbors. 1 for fcc structure, see figure 3.4(b).
Figure 3.5. Signatures of the local environments identified in the CNA for hcp structure [1] with 12 nearest neighbors (NN). (a) Starting configuration for hcp crystal structure with 12 NNs for central red \(i\) atom surrounded by 12 (red and brown) atoms. Pair of nearest neighbor atoms is indicated by red atoms \(i\) and \(j\). All other red atoms are the common neighbors of the \(i-j\) pair and brown atoms are the other atoms in the hcp structure but not shared neighbors of \(i-j\) pair. (b) 422 structure with pair \(i-j\) and its common neighbors isolated from hcp structure. The three indices 4, 2, and 2 represent the hcp structure in Atomistic simulations. Refer to the text for the description of these indices.

Based on these indices, figure 3.4 and 3.5 shows the CNA signatures for the fcc and hcp crystal structures. The relative fraction of each of these is shown in table 3.1. 421 and 422 are found in the fcc and hcp structures. The other indices, not shown here, 441 and 661 are found in the bcc structure.
Table 3.1. Fraction of CNA diagrams present in fcc, hcp and bcc crystal structures [1].

<table>
<thead>
<tr>
<th>CNA diagram</th>
<th>fcc</th>
<th>bcc</th>
<th>hcp</th>
</tr>
</thead>
<tbody>
<tr>
<td>421</td>
<td>1</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>422</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>441</td>
<td>0</td>
<td>(\frac{3}{7})</td>
<td>0</td>
</tr>
<tr>
<td>661</td>
<td>0</td>
<td>(\frac{4}{7})</td>
<td>0</td>
</tr>
</tbody>
</table>

3.7. Atomistic Simulations code and Visualization tools

LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) code [110] is used for classical MD simulations. MedeA [79, 111] is used for DFT calculations. OVITO (Open Visualization Tool) [112] and VESTA [113] are used for visualization and analysis of atomistic simulation data.

3.8. Summary

This chapter described the MD simulation methodology I use in this dissertation to do atomistic simulations. I also briefly described the DFT methodology, which will be used for stacking fault energy calculations. It also discussed the property calculations and structure identification from MD simulations and mentions the Atomistic tools used to carry out and analyze the results.
In this chapter, I will first explain the CD-EAM formalism to create binary pair potential and then show the actual steps implemented to develop a Mg-Li potential.

4.1. Introduction to CD-EAM potentials

Atomistic simulations require a potential describing interatomic interactions correctly. These potentials are often fit to equilibrium lattice constants, cohesive energy, forces, and other properties such as heat of formation, elastic constants, and vacancy formation energy obtained experimentally or from ab initio calculations. The robustness of these potentials to reproduce different properties beyond the fitting database used is termed as transferability.

As discussed in the previous chapter, the energy for metallic systems in MD is a function of interaction distance and is commonly described by the Embedded Atom method (EAM) based on density-functional theory [90, 91, 92] ideas or the Finnis-Sinclair approach developed from second-moment tight-binding [93] formalisms. In EAM formalisms, energy of a mono component metal is expressed as,

\[
E = \frac{1}{2} \sum_{i,j(i\neq j)} V_{ij}(r_{ij}) + \sum_i F_i(\sum_{i\neq j} \rho_i(r_{ij}))
\]

Where, \( V \) is an electrostatic two-body interaction describing the energy of the pair interaction between atoms at sites \( i \) and \( j \). \( F_i \) is the embedding energy obtained by embedding an atom \( i \) into the local electron density provided by the remaining atoms \( j \) of the system. \( \rho \) is the spherically or non-spherically averaged atomic electron density and is calculated for each atom by superpositioning of atomic density from other atoms.

In the EAM ansatz, the energy of a binary alloy with two elements A and B, \( E_{AB} \), is given as,
\[
E_{AB} = \frac{1}{2} \sum_{i,j(i\neq j)} V_{A_iB_j}(r_{ij}) + \sum_i F_i(\sum_{i\neq j} \rho_{A_iB_j}(r_{ij}))
\]

Where, \(A\) and \(B\) are two elements at site \(i\) and \(j\), \(F\) is the embedding functions for either type of elements and \(V\), and \(\rho\) are pair potentials and densities between \(A-B\) pairs. Thus, the alloy properties are described by \(V_{AB}\) and \(\rho_{AB}\). The EAM ansatz for binary alloys is often fitted to dilute heat of solution or to properties of a particular intermetallic phase [114, 115]. The alloy potentials determined this way are not reliable for concentrated alloys. Furthermore, they work well for systems with positive enthalpy of mixing over the entire concentration range [116, 114, 117, 118]. In addition, alloys such as Fe-Cr or Pd-Ni that show a strong asymmetry or a sign of inversion in the heat of formation, are not well described by traditional EAM many body potentials.

Caro et al. [9] developed a concentration dependent embedded atom method (CD-EAM) model to address these issues and successfully applied it to Fe-Cr system [9] for which the heat of mixing (HOM) is positive over the composition range and shows a sign of inversion as seen in figure 4.1. CD-EAM formalism works well for concentrated alloys, skewed or a system with sign of inversion in heat of formation. It was successfully applied to study thermodynamic properties of Fe-Cr [9, 10, 67, 68, 69, 70], Cu-Nb [71], and Pb-Li alloys [72, 73]. It has also been shown that the computational cost of CD-EAM is only slightly larger (1.5 to 1.7 times) than conventional EAM potentials, which makes it efficient to use. I have used CD-EAM method to develop a Mg-Li alloy potential to study thermodynamic and mechanical properties.

4.2. CD-EAM formalism

Equation 33 [9, 10] is the starting point for CD-EAM formalism. In this equation, cross pair potential is given by \(V_{AB}\) and \(\rho_{AB}\) between \(A\) and \(B\) elements. Note that both the cross pair interaction terms \(V_{AB}\) and \(\rho_{AB}\) in this equation are function of distance \(r_{ij}\) only. CD-EAM implements the composition term \(X\) as discussed in this section. To create the cross-pair interaction contributions of both \(V_{AB}\) and \(\rho_{AB}\) can be used. However, the
Figure 4.1. The Fe-Cr CD-EAM binary potential reproduces heat of mixing \((\Delta h)\) as a function of Fe composition [9]. Note that Fe-Cr CD-EAM potential reproduces the \(\Delta h\), which is positive over entire range, and shows a sign of inversion near \(X_{Fe} = 1\). Previous potential formalisms do not work well for such systems.

The total smearing model [119] gives the functional form for the energy of mixing. In this model, the species at site \(i\) can be either A or B type element, but both are embedded in the same environment as,

\[
\rho_{\alpha} = \rho_{\alpha}^0 / \rho_{\alpha,eq}^0
\]

\[
F_{\alpha}(\rho_{\alpha}) = F_{\alpha}^0(\rho_{\alpha}^0) - F_{\alpha}^{0'}(\rho_{\alpha,eq}^0)\rho_{\alpha}^0
\]

\[
V_{\alpha,\alpha}(r) = V_{\alpha,\alpha}^0(r) + 2F_{\alpha}^{0'}(\rho_{\alpha,eq}^0)\rho_{\alpha}^0(r)
\]  

(34)

Where, \(^0\) stands for the original functions and \(\rho_{\alpha,eq}^0 = \sum_{j \neq i} \rho_{\alpha_i}(r_{eq}^{ij})\) is the density on an atom site in the equilibrium lattice. The effective representation transformations do not alter the cross pair properties of the alloy but allows us to combine two arbitrary elements with unrelated magnitudes of electron densities.

The total smearing model [119] gives the functional form for the energy of mixing. In this model, the species at site \(i\) can be either A or B type element, but both are embedded in the same environment as,
\[
E^{rand} = x_A^2 \sum V_{AA}(r_{ij}) + x_B^2 \sum V_{BB}(r_{ij}) + 2x_Ax_B \sum V_{AB}(r_{ij}) + x_A F_A(\bar{\rho}) + x_B F_B(\bar{\rho})
\]

(35)

Where, \( \bar{\rho} = x_A \sum \rho_A(r_{ij}) + x_B \sum \rho_B(r_{ij}) \) and \( x \) is composition.

The effective representation in equation 34 contributes embedding energy term to the total energy of the alloy negligible ( 1 meV/atom) as compared to the total magnitude of tens of meV/atom. Thus, pair potential interaction is the sole contributor to the formation energy.

For a binary alloy, we can substitute \( x = x_A, (1 - x) = x_B, \nu_A = \sum V_{AA}(r_{ij}), \nu_B = \sum V_{BB}(r_{ij}) \) and \( \nu_{AB} = \sum V_{AB}(r_{ij}) \) into Eq. (35) and simplify the embedding energy terms, to get the energy of mixing as,

\[
\Delta E^{pair} = x(1 - x)\{2\nu_{AB} - (\nu_A + \nu_B)\}
\]

(36)

The \( V_{AB}(r_{ij}) \) term included in \( \nu_{AB} \) depends on both composition \( (x) \) and distance \( (r) \) as:

\[
V_{AB}(x,r) = h(x)[aV_{AA}(r) + bV_{BB}(r)]
\]

(37)

Where \( aV_{AA}(r) + bV_{BB}(r) \) is the initial guess of the cross pair potential and is taken as the weighted sum of the two pure elemental pair potentials. \( a \) and \( b \) are the fractions of pair interaction terms of either \( A \) or \( B \) type elements. The \( h(x) \) term is a polynomial function that serves as a prefactor for the cross pair potential and modifies the energy of the interaction as a function of the local concentration. The \( h(x) \) term makes the CD-EAM formalism composition dependent and differentiates it from previous pair formalisms. The formation energy of the cross pair potential is given as the combination of equations (36) and (37) as,
The coefficients of the polynomial $h(x)$ is determined by numerically fitting equation (38) to heat of mixing $\Delta H^{\text{mix}}$ from the CALPHAD (Calculation of Phase Diagrams) data as a target function. $\Delta H^{\text{mix}}$ from the CALPHAD model is taken as a Redlich-Kister expansion [120],

$$
\Delta H^{\text{mix}} = x(1-x) \sum_{p=0,n} L_p(1-2x)^p
$$

Where, $L_p$ is the $p$th order binary interaction parameter.

The $h(x)$ function can be found by minimizing the difference between energy from the cross pair potential (Eq. (38)) and $\Delta H^{\text{mix}}$ (Eq. (39)), as,

$$
\{2h(x)(a\nu_A + b\nu_B) - (\nu_A + \nu_B)\} \simeq \sum_{p=0,n} L_p(1-2x)^p
$$

Once we get the $h(x)$ function, the energy of a binary alloy system in CD-EAM formalism can be written as,

$$
E_{AB} = \frac{1}{2} \sum_{i,j(i\neq j)} h_{A,B_j}(x)V_{A,B_j}(r_{ij}) + \sum F_i(\sum_{i\neq j} \rho_{A,B_j}(r_{ij}))
$$

Note here that the cohesive energy in CD-EAM formalism takes into account the contribution of composition of concentrated alloys as $h_{A,B_j}(x)$ and also keeps the distance function $r_{ij}$ of the earlier formalism intact.

Enabling the concentration dependent behavior requires the ability to calculate the local composition at an atomic site. Here, partial B density, the component of total density at atoms $i$ and $j$ due to B atoms at neighboring sites $l$, is used to calculate the composition. The density $\rho_i$ on a lattice site $i$ is given by the sum over the neighbors $l \sum_l \rho_{\beta}(r_{il})$, where $\beta$ is for either elements A or B occupying site $l$. The sum is divided into the partial contributions
as, \( \varrho_i = \sum'_l \rho_A(r_{il}) + \sum''_l \rho_B(r_{il}) = \varrho_i^A + \varrho_i^B \), where the \( ' \) indicates neighbors of \( i \) occupied by A-type atoms and \( '' \) is neighbors of \( i \) occupied by B-type atoms. The composition used in a pair term involving sites \( i \) and \( j \) is defined as,

\[
(42) \quad x_{i,j} = \frac{1}{2} (x_i + x_j) = \frac{1}{2} \left( \frac{\varrho_i^B}{\varrho_i} + \frac{\varrho_j^B}{\varrho_j} \right)
\]

Figure 4.2 illustrates the calculation of composition for concentrated alloys [10].

**Figure 4.2.** Calculation of the composition \( X \) of the alloying element is shown in this figure [10]. \((x)\) function gives the concentration dependent properties for the A-B type alloy. Dotted circles indicates the cutoff of the potential. The concentration for atom 1, \( X_{1(2)}^A \), is calculated by taking the ration of number of atoms of same type divided by all the atoms within the cutoff defined by the dotted circular area. Same method is applied to calculate the concentration of atom 2 which is of type B.
4.3. Mg-Li CD-EAM potential creation

Figure 4.3 schematically shows the steps followed to create a Mg-Li interatomic potential. I start with single element EAM potentials for Mg and Li and first make an initial guess of the cross-pair potential. Next, we numerically fit with a target function to obtain the cross-pair interaction for Mg-Li system. As shown in figure 4.3 schematically, the initial guess of the cross-pair potential depends only on distance \( r_{ij} \), but the final cross pair potential also takes into account the composition term \( h(x) \). I will detail these steps next.

Mg-Li CD-EAM potential construction steps

\[
E = \sum_{i}^{N} \left[ (F_i \sum_{j \neq i} \rho_i (r_{ij})) + \frac{1}{2} \sum_{j \neq i} V_{ij}(r_{ij}) \right]
\]

\[
\phi_{AB}(r_{ij}) = \frac{1}{m} V_{AA}(r_{ij}) + \frac{1}{n} V_{BB}(r_{ij})
\]

Depends on distance \( r_{ij} \) only

\[
x(1-x)\{2V_{AB} - (V_{AA} + V_{BB})\} \approx \Delta H^{\text{mix}}
\]

\[
V_{AB}(x_{ij}, r_{ij}) = h(x_{ij}) \phi_{AB}(r_{ij})
\]

Depends on distance \( r_{ij} \) and composition \( x_{ij} \)

1. EAM Formalism
   Effective Representation

2. Initial Guess of
   Cross Pair Potential

3. Numerical fitting wrt target
   Heat of Mixing to get \( h(x) \)

4. Final Cross Pair
   Potential

Figure 4.3. Summary of the steps to create Mg-Li cross-pair potential. \( AA \), \( BB \), and \( AB \) are the interaction between Mg-Mg, Li-Li and Mg-Li atoms respectively. \( V \) represents the pair interaction term from the EAM equation. \( \phi \) is the initial guess of the cross-pair potential and \( h(x) \) represents the function which makes the cross-pair interaction concentration dependent.
4.3.1. *EAM potentials for pure Mg and Li*

In this work we use the two pure elemental potentials for Mg [11] and Li [12] available in the literature to develop the cross pair interaction of Mg-Li binary alloy. Two EAM potentials are available in the literature for both pure Mg and Li. Here, I will discuss why I chose a specific EAM potential for each of the element.

<table>
<thead>
<tr>
<th>Property</th>
<th>Mg EAM potential, Sun2006 et al</th>
<th>Literature*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Constant a (hcp), Å</td>
<td>3.184</td>
<td>3.186</td>
</tr>
<tr>
<td>Lattice Ratio c/a (hcp), Å</td>
<td>1.628</td>
<td>1.622</td>
</tr>
<tr>
<td>Cohesive Energy, eV/atom</td>
<td>-1.529</td>
<td>-1.51</td>
</tr>
<tr>
<td>Vacancy Formation Energy, eV</td>
<td>0.90</td>
<td>0.88</td>
</tr>
<tr>
<td>Melting Point, K</td>
<td>914 +/-3</td>
<td>923</td>
</tr>
<tr>
<td>Bulk Modulus, GPa</td>
<td>38</td>
<td>37</td>
</tr>
<tr>
<td>Elastic Constant, C11, GPa</td>
<td>69.6</td>
<td>63.5</td>
</tr>
<tr>
<td>Elastic Constant, C12, GPa</td>
<td>25.3</td>
<td>26</td>
</tr>
<tr>
<td>Elastic Constant, C44, GPa</td>
<td>12.8</td>
<td>18.4</td>
</tr>
<tr>
<td>Elastic Constant, C13 GPa</td>
<td>16</td>
<td>21.7</td>
</tr>
<tr>
<td>Elastic Constant, C33 GPa</td>
<td>69.5</td>
<td>66.5</td>
</tr>
<tr>
<td>$\Delta E_{\text{fcc}\to \text{hcp}}, \text{eV/atom}$</td>
<td>0.012</td>
<td>0.013</td>
</tr>
<tr>
<td>$\Delta E_{\text{bcc}\to \text{hcp}}, \text{eV/atom}$</td>
<td>0.014</td>
<td>0.029</td>
</tr>
</tbody>
</table>

**Figure 4.4.** Properties of Pure Mg EAM potential [11] used in this study.

*All the values are taken from [11].

For Mg, the first EAM potential was developed by Liu et al. in 1996 using the force-matching method [121]. This potential reproduces lattice constant, cohesive energy, elastic constants, vacancy formation energy and activation energy of self diffusion in hcp lattice well. But, Sun et al. [11] found that Liu 1996 potential underestimates the melting point of hcp Mg by 180K and that the hcp phase transforms to bcc before melting contrary to the available experimental data. To eliminate these problems, Sun et al. [11] modified this potential in 2006 by combining force-matching method with an approach for fitting equilibrium melting temperatures proposed by Sturgeon and Laird [122]. The properties of
the potential developed by Sun et al. is shown in figure 4.4. This figure shows that properties including $T_m$ match the literature values well. However, this potential underestimates the values for elastic constants (C44, C13) and the phase transformation energy between bcc and hcp phase. Both these potentials were used by Yasi et al. [123], and they found that Sun’s potential agrees with first principles calculations for basal and prismatic stacking faults better than Liu et al. potential. Therefore, in this study we use new potential developed by Sun et al., which shows the correct phase stability and stacking fault energy for basal and prismatic planes.

<table>
<thead>
<tr>
<th>Property</th>
<th>Li EAM potential, Derlet 1999</th>
<th>Literature*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Constant, Å</td>
<td>3.52</td>
<td>3.5</td>
</tr>
<tr>
<td>Cohesive Energy, eV</td>
<td>-1.645</td>
<td>-1.65</td>
</tr>
<tr>
<td>Vacancy Formation Energy, eV</td>
<td>0.52</td>
<td>0.52-0.66</td>
</tr>
<tr>
<td>Elastic Constant, C11, GPa</td>
<td>17.83</td>
<td>14.8</td>
</tr>
<tr>
<td>Elastic Constant, C12, GPa</td>
<td>14.41</td>
<td>12.5</td>
</tr>
<tr>
<td>Elastic Constant, C44, GPa</td>
<td>12.19</td>
<td>10.8</td>
</tr>
<tr>
<td>Melting Point, K</td>
<td>430</td>
<td>450</td>
</tr>
</tbody>
</table>

Figure 4.5. Properties of Pure Li EAM potential [12] used in this study. *All the values are taken from [12]. Bold values are calculated as part of present study and were not given in the original paper. *All values are taken from Derlet et al. [12].

Two EAM potentials are available in the literature for Li, as well. First developed by Derlet et al. in 1999 [12] to study the vacancy formation in bulk Li and second developed by Belaschenko et al. [124] in 2009 to specifically study the liquid Li. Belaschenko et al. potential does not reproduce the solid properties such as lattice constants, elastic constants, and cohesive energy well like the Derlet et al. potential as shown in figure 4.5.
Figure 4.6. Pair interaction terms for pure Mg and Li are taken from the literature [11, 12]. Effective representation curves of $V_{Mg}$ and $V_{Li}$ are used to create Mg-Li cross-pair potential term $V_{Mg-Li}$. Effective representation for individual pair potentials is achieved by using equation 34.

4.3.2. Effective representation of the single element Mg and Li EAM potentials

The individual potentials are taken from different sources with very different and unrelated magnitudes of electron densities. So, we use mathematical transformations shown in equation 34 to reduce the contribution of embedding energy term to total cohesive energy. This transformation makes the total energy of the pure element to depend largely on pair interaction terms and allows us to create cross pair potential based on only pair interaction term. Figure 4.6 shows the properties of pair interaction terms taken from literature [11, 12] and after applying effective representation formulation. I will use the effective representation terms for Mg and Li to create a cross-pair interaction term $V_{Mg-Li}$. The minimum for the $V_{Mg}$ and $V_{Li}$ corresponds to cohesive energy and lattice constant values.
Figure 4.7. Figure shows the embedding energy term contribution to HOM for hcp and bcc phases after applying the effective representation of the pure elemental Mg and Li potentials. The embedding energy contribution to HOM is negligible (0 eV/atom) as compared to high contribution of pair potential term and target HOM for both phases shown later in figure 4.9. Therefore, embedding energy term can be neglected for cross-pair interaction of Mg-Li alloy.

I have shown the contribution of embedding energy and pair potential terms to HOM in figures 4.7 and 4.9 for hcp and bcc phases. As seen in these figures, the contribution of embedding energy to HOM is negligible as compared to pair potential terms.

4.3.3. Inputs and Targets for Mg-Li CD-EAM potential

In addition to the pure Mg and Li EAM potentials and their properties, I also use lattice constants as a function of Li concentration as input to create the Mg-Li binary potential. Experimental values of the lattice parameters [13] are shown in figure 4.8(a), dotted lines show an extrapolation beyond the concentration where equilibrium phase is stable. Figure 4.8(b) shows the target $\Delta H^{mix}$ functions taken from CALPHAD (Calculation
of Phase Diagram) data published in Saunders et al. [4]. I attempt to fit the cross-pair potential to the $\Delta H^{mix}$ to reproduce the Mg-Li phase diagram.

### 4.3.4. Initial guess of the cross pair potential

The average of pure Mg and Li pair potentials is taken as a starting point for cross-pair potential. I took $\phi_{Mg-Li}(r) = \frac{1}{4}V_{Mg} + \frac{7}{4}V_{Li}$ as the starting guess of the cross-pair potential. This initial guess is later modified by numerical fitting to a the target function. $\frac{1}{4}$ and $\frac{7}{4}$ are taken based on the trial and error method. I tried several other combinations such as $\frac{1}{2}$ for both pair terms, but using above mentioned fractions gave the best starting point for the numerical fitting and also the final properties of the potential are in better agreement with literature. The initial guess of the cross-pair potential is shown in figure 4.10(a).
Figure 4.9. HOM for the hcp and bcc phases from initial guess of the Mg-Li cross pair potential is considerably different than target literature values. It is difficult to numerically fit both phases with single $h(x)$ function. Therefore, an intermediate fitting modifies the initial guess of the cross-pair potential and brings the HOM closer to target values.

4.3.5. **Numerical fitting to modify the initial guess of the cross pair potential and generate $h(x)$ function**

Now, I numerically fit the initial guess of the cross-pair potential in two steps described below. In the first step, the numerical fitting is done to modify the initial guess of the cross-pair potential. This step accommodates the large difference in $\Delta H_{mix}$ for hcp and bcc phases seen in figure 4.8(b). As shown in figure 4.9, the HOM from the initial guess also differs considerably from the literature values. It is difficult to match the two different $\Delta H_{mix}$ target functions with the $h(x)$ function. So, we modify the initial guess by numerical fitting shown in equation 43 to bring the HOM’s from initial guess closer to target functions.

\[
x(1-x)2\phi_{Mg-Li} - (V_{Mg} + V_{Li}) \simeq \Delta H_{mix}
\]
Now, a second numerical fitting is done to get the \( h(x) \) function as shown in equation 44.

\[
x(1 - x)2V_{Mg-Li} - (V_{Mg} + V_{Li}) \approx \Delta H^{mix}
\]

Where, \( V_{Mg-Li} = h(x)\phi_{Mg-Li} \) is the final cross pair potential.

**Figure 4.10.** Figure shows the properties after (a) first numerical fitting- Initial guess of the cross pair potential, modified cross pair potential along with the individual pair interaction terms for Mg and Li. (b) Second numerical fitting - \( h(x) \) function.

The second fitting gives the \( h(x) \) function and matches the \( \Delta H^{mix} \) from \( V_{Mg-Li} \) with the target values. Figure 4.10(a) shows the pair potential values for individual elements, initial and modified guess of the cross-pair potential, while 4.10(b) depicts \( h(x) \) functions. Table 4.1 shows the spline function used to describe cross-pair potential and the quadratic equation used for \( h(x) \) function. Figure 4.11 shows the \( \Delta H^{mix} \) from the final cross-pair potential \( V_{Mg-Li} \), and \( h(x) \) function, and compares it with target values. As seen in this
Figure 4.11. Figure compares the $\Delta H^{\text{mix}}$ for the final cross pair potential with the target value.

In this chapter, I first explained the CD-EAM origins and its formalism. Then I applied the CD-EAM formalism to create a binary Mg-Li CD-EAM potential. The reliability and transferability of this potential is discussed in next chapter.
Table 4.1. Cross pair potential function and $h(x)$ function for Mg-Li CD-EAM potential. Spline function is used for cross-pair potential description and quadratic equation describes $h(x)$ function.

<table>
<thead>
<tr>
<th>Function</th>
<th>Value</th>
<th>Cutoffs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V(r)$</td>
<td>$[-0.0102213(r)^2(r - 2.68129)](r - 7.5)^2$</td>
<td>0-2.5</td>
</tr>
<tr>
<td></td>
<td>$[-0.00352367(r - 2.5)^2(r - 30.311)](r - 7.5)^2$</td>
<td>2.5-3.8</td>
</tr>
<tr>
<td></td>
<td>$[+0.00943653(r - 3.8)^2(r - 2.67645)](r - 7.5)^2$</td>
<td>3.8-4.6</td>
</tr>
<tr>
<td></td>
<td>$[-0.00217717(r - 4.6)^2(r - 10.3151)](r - 7.5)^2$</td>
<td>4.6-5.2</td>
</tr>
<tr>
<td></td>
<td>$[+0.0169171(r - 5.2)^2(r - 5.52108)](r - 7.5)^2$</td>
<td>5.2-6.2</td>
</tr>
<tr>
<td></td>
<td>$[-0.0122586(r - 6.2)^2(r - 11.2989)](r - 7.5)^2$</td>
<td>6.2-7.5</td>
</tr>
<tr>
<td>$h(x)$</td>
<td>$1.00029 - 0.00215437x + 0.205351x^2 - 0.472254x^3 + 0.254323x^4$</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER 5

VALIDATION OF MG-LI CD-EAM POTENTIAL

In this chapter, I will verify the reliability and transferability of the newly created Mg-Li CD-EAM potential by calculating different properties of the alloy and comparing it with available literature data. I used LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) molecular dynamics (MD) code [110] for my calculations. Heat of mixing, bulk modulus, and stacking fault energy are calculated at 0K as a function of concentration. Lattice constants and free energy calculations of the phase stability are done at 0K and at higher temperatures as well. In this chapter, I present the results for stacking fault energy of basal and prismatic planes. The stacking fault energy for pyramidal plane and twin fault energies (tension and compression twin) are presented as part of chapter 7.

5.1. Free energies calculations and phase diagram creation

Free energy calculations and phase diagram creation will predict the phase stability as a function of temperature and concentration for newly created Mg-Li CD-EAM potential. Therefore, I start the verification of the properties by calculating the free energy and phase diagram. Once the phase boundaries on the Mg-Li phase diagram are known, the effect of alloying additions on different properties can be studied in hcp and bcc phases. To the best of my knowledge, this is the first attempt to create phase diagram for the Mg-Li system using atomistic simulations.

The phase diagram is created from the common tangent construction of free energies of solid and liquid phases. The Mg-Li system contains two solid phases hcp and bcc. Therefore, to generate the phase diagram, I first describe the free energy calculation methodology (for pure elements and alloys), and use it for Mg-Li alloys. I follow the following methodology described in the literature [125, 126, 118] to calculate free energy and phase diagram using atomistic simulations.

Some of the sections in this chapter are reproduced from my paper published in Computational Materials Science, Karewar et al. [49], with permission from Elsevier.
5.1.1. *Free energy calculations for pure Mg and Li elements*

The free energy per particle is determined by the thermodynamic integration between the state of interest at temperature \( T \) and a reference state at temperature \( T_0 \) with known free energy \( f(T_0) \). The free energy per particle is given by the Gibbs-Duhem equation as shown in equation 45. This equation is a thermodynamic integration between the state of interest at temperature \( T \) and a reference state at temperature \( T_0 \) with known free energy \( f(T_0) \).

\[
\begin{align*}
    f(T) &= f(T_0) \frac{T}{T_0} - T \int_{T_0}^{T} \frac{h(\tau)}{\tau^2} d\tau
\end{align*}
\]

where, \( h(\tau) \) is the enthalpy per atom. \( \tau \) is the temperature that varies from initial temperature \( T_0 \) to final temperature \( T \).

The switching Hamiltonian method is used to calculate the reference free energy \( f(T_0) \) [127]. Hamiltonian, \( H \), shown in equation 46 is used to calculate the free energy difference between \( U \) (actual EAM Hamiltonian) and \( W \) (reference system with known free energy) by calculating the reversible work required during the process of switching from one to other. This switch is reversible and free of any phase transitions.

\[
\begin{align*}
    H &= (1 - \lambda)W + \lambda U
\end{align*}
\]

Here, \( \lambda \) is the switching or coupling parameter that changes from 0 (for \( W \)) to 1 (for \( H \)).

The free energy \( f(T_0) \) and \( U \) terms in equations 45 and 46 are given by the following equations 47 and 48.

\[
\begin{align*}
    f(T_0) &= f_W(T_0) + \Delta f_1
\end{align*}
\]
\( \Delta f_1 = \frac{1}{N} \int_0^1 \left\langle \frac{\delta H}{\delta \lambda} \right\rangle d\lambda = \frac{1}{N} \int_0^1 \langle U - W \rangle \)

Here, \( f_W(T_0) \) is the free energy of the reference system at temperature \( T_0 \). The integration is carried by varying the coupling parameter \( \lambda \) between 0 and 1, and \( \langle ... \rangle \) is the canonical ensemble average or time average in a \( (T, V, N) \) MD simulation.

Now, I will describe how to calculate the free energy of the reference system \( f_W(T_0) \) for solids and liquids. The calculations involve different reference systems for solids and liquids.

For solids, the reference system \( W \) is taken as the set of Einstein oscillators centered on the average positions of the atoms in the \( (T_0, P = 0, N) \) ensemble corresponding to the Hamiltonian \( U \). The non-interacting Einstein oscillators with no internal pressure are given by the ensemble \( (T, V, N) \). Now, the free energy per particle of the Einstein crystal is given by equation 49 [128].

\[
(49) \quad f_{W}^{sol}(T_0) = f_{Eins}(T_0) = -3k_B T_0 \ln \left( \frac{T_0}{T_E} \right)
\]

Here, \( k_B \) is the Boltzmann constant, \( T_E = \frac{h \omega}{k_B} \) is the Einstein temperature where \( h \) is the Plank constant divided by 2, and \( \omega \) is the frequency of the oscillations. The Einstein temperature \( T_E \) is chosen to make the integral in equation 48 as smooth as possible to improve the numerical efficiency. Once the free energy of the reference solid state is known from equation 49, the free energy difference \( \Delta f_1 \) can be calculated by varying the coupling parameter from 0 to 1 as shown by equation 48.

For liquids, an ideal gas at the same temperature and volume of the EAM sample is taken as the reference system \( W \). The coupling parameter \( \lambda \) varying between 0 and 1 is used as in the case of solids to calculate the free energy difference between the EAM potential system \( U \) and a system with repulsive potential \( W_L \), here, \( W_L = 0.1U^{rep} \). Here, \( U^{rep} \) is the purely repulsive part of the pair potential of the EAM. This repulsive part is lower in magnitude (0.1) to avoid the crystallization of the sample, which is an irreversible process.
The free energy change for liquid pure elements is given by switching integration, $\Delta f_1$, as in the case of solid switching by equation 48. The equilibrium volume $V_0$ at $T_0$ and $P=0$ that equilibrates the Hamiltonian of EAM system $U$ is used for the switching of ideal gas. The switching from $U$ to $W$ has an intermediate step to avoid the particle overlap during integration. In this step, a reversible expansion of the repulsive gas at $V_0$ and high pressure is carried out to reach the dilute limit so that it becomes identical to the ideal gas. This is followed by the reversible compression of the ideal gas to recover the initial density or volume. The change in free energy for both the processes is given as $\Delta f_2$ in equation 50.
\[ \Delta f_2 = k_B T_0 \int_0^{\rho_0} \left[ \frac{P}{\rho k_B T_0} - 1 \right] \frac{d\rho}{\rho} \]

Where \( \rho_0 \) is the particle density given as \( \frac{N}{V_0} \). The free energy of the ideal gas at \((T_0, \rho_0)\) obtained by the above two-step process is given as \( f_{W}^{liq} \) shown in equation 51.

\[ f_{W}^{liq}(T_0, \rho_0) = f_{ideal}(T_0, \rho_0) = k_B T_0 \left[ \ln(\rho_0 \Lambda^3) - 1 \right] \]

Where \( \Lambda^2 = \frac{\hbar^2}{2\pi m k_B T_0} \) is the de Broglie wavelength, \( \hbar \) is the Plank constant, and \( m \) is the atomic mass.

Now, the free energy of the liquid phase is given as the combination of \( \Delta f_1, \Delta f_2, f_{W}^{liq} \) as,

\[ g_L(T_0) = \Delta f_1 + \Delta f_2 + f_{W}^{liq}(T_0, \rho_0) \]

Thus, the free energy of solid and liquid phases of the pure elements is given by the equations 45, 47, and equation 52.

Finally, the melting points of the pure elements is given by the intersection point of solid and liquid phase free energy curves.

5.1.2. Free energy calculations for Mg-Li alloys

The Mg-Li experimental phase diagram has hcp, bcc and liquid phases. To calculate the free energies for each of these phases, first a set of free energy versus temperature function, \( g_c(T) \), is constructed. From \( g_c(T) \), we obtain free energy versus composition \( (g_T(c)) \) curves at different temperatures for all three phases. The common tangent construction in \( g_T(c) \) will give the phase boundaries in the Mg-Li phase diagram.

Equations 45 to 52 are used to calculate the free energy as a function of temperature, \( g_c(T) \), for range of alloy compositions. RHS of equation 45, enthalpy per atom at temperature \( T \) is calculated by heating or cooling the samples at temperature \( T \). The free energy of mixing
Figure 5.2. Schematic diagram of liquid phase Hamiltonian switching between CD-EAM crystal and Ideal gas by varying $\lambda$ to calculate $g_L(T_0)$ in equation 52.

For reference configurations, $f_{\text{Eins}}$ and $f_{\text{ideal}}$ used in equation 45, are given by equations 53 and 54 [127].

\begin{align*}
(53) \quad f_{\text{Eins}}(c, T_0) &= cf_{\text{Eins}}^{\text{Mg}} + (1 - c)f_{\text{Eins}}^{\text{Li}} - T_0S_{\text{conf}} \\
(54) \quad f_{\text{ideal}}(c, T_0, \rho) &= cf_{\text{ideal}}^{\text{Mg}} + (1 - c)f_{\text{ideal}}^{\text{Li}} - TS_{\text{conf}}
\end{align*}

Where $c$ is the Mg concentration, $f_{\text{Eins}}^{\text{Mg}}, f_{\text{Eins}}^{\text{Li}}, f_{\text{ideal}}^{\text{Mg}},$ and $f_{\text{ideal}}^{\text{Li}}$ are given by equations 49 and 51. $S_{\text{conf}}(c)$ is the configuration entropy given as $-k_B [c\ln(c) + (1 - c)\ln(1 - c)]$, assuming the solution is completely random. $\rho$ is the total density, and $\rho_{\text{Mg}} = c\rho$ and $\rho_{\text{Li}} = (1 - c)\rho$ are the partial densities for Mg and Li respectively.
5.1.3. Summary of the free energy calculations

In this sub-section, I list the steps described to calculate the free energy of pure Mg, pure Li, and Mg-Li alloys.

(1) Determine the enthalpy \((H)\) versus \(T\) relation using MD simulations for pure elements and alloys of different compositions in all the phases.

(2) Fit a second-order polynomial to enthalpy curves as

\[
h^\Phi(c, T) = a^\Phi c + b^\Phi c T + c^\Phi c T^2
\]

\(a, b,\) and \(c\) are the coefficients of polynomial fitting. \(\Phi\) denotes either solid or liquid phase.

(3) Calculate the Gibbs-Duhem integral in equation 45 as,

\[
-T \int_{T_0}^{T} \frac{h^\Phi(c, T)}{\tau^2} d\tau = a^\Phi c - b^\Phi c T \ln(T) - c^\Phi c T^2 + d^\Phi c T.
\]

\(d\) is the coefficient of polynomial fitting.

(4) Calculate Switching Hamiltonian integral for solids (hcp and bcc phases) and liquid, \(\langle U - W \rangle\), at different compositions of alloy.

(5) Evaluate \(\Delta f_1\) by analytic integration of sixth order polynomial fits to \(\langle U - W \rangle\).

(6) Approximate adiabatic expansion of the repulsive fluid, equation 51, at each composition.

(7) Evaluate \(\Delta f_2\) by sixth order polynomial fits to integral in equation 51.

(8) Fit second order polynomial to coefficients \(a^\Phi(c), b^\Phi(c), c^\Phi(c),\) and \(d^\Phi(c)\) as a function of composition.

These steps give a general equation for free energy of the each phase, \(\Phi\), as a function of composition as given in the equation 57.

\[
g^\Phi(c, T) = a^\Phi(c) - b^\Phi(c) T \ln(T) - c^\Phi(c) T^2 + d^\Phi_G(c) - TS_{\text{conf}}(c)
\]

Where, \(d^\Phi_G(c) = d^\Phi(c) + \frac{1}{T} g^\Phi(c, T_0)\)
5.2. Mg-Li CD-EAM potential free energy calculations and phase diagram creation

Free energy calculations use 800 atoms for the hcp phase and 686 atoms for the bcc phase. For alloys with different compositions and random configurations, the fluctuations in energy values are of a few meV/atom which is less as compared to eV/atoms values of the free energies. Therefore the above mentioned system sizes and one reference configuration for hcp and bcc phases are adequate for statistical averaging. In all the simulations, Nose-Hoover thermostat and Parinello-Rehman algorithm is used to control temperature and pressure respectively [104]. The timestep used is 2 fsec. Now, I will discuss the MD simulations based on the steps summarized in subsection 5.1.3.

The first step is to determine coefficients $a^\Phi_c, b^\Phi_c, c^\Phi_c,$ and $d^\Phi_c$ from fit to $H$ versus $T$ relation. In this step, samples for Mg and Li solid phases are heated in successive runs from 0K to 1200K and cooled down again to 0K temperature at intervals of 50K for the hcp phase and 25K for the bcc phase. Samples are first equilibrated for $10^4$ steps and then the statistical average of thermodynamic ensembles is performed over the next $10^4$ steps. Enthalpy per particle for solids($h_s$) and liquids ($h_l$) is obtained during both heating and cooling runs. Second order polynomials are fitted to obtain the coefficients $a^\Phi_c, b^\Phi_c, c^\Phi_c,$ and $d^\Phi_c$. These coefficients are calculated for different Li concentrations for each phase as shown in equation 56. A third order polynomial is fitted to get these coefficients as a function of concentration, $a^\Phi(c), b^\Phi(c), c^\Phi(c),$ and $d^\Phi(c)$, shown in equation 57. Note that in the original CD-EAM formalisms second order polynomials are fitted [118, 126, 129], whereas I fit third order polynomials to improve the fit for the phase diagram calculations. The enthalpy per particle during heating and cooling is shown in figure 5.3. The non-linear increase in enthalpy during heating and cooling runs are the temperatures at which solid melts and liquid solidifies.

The next step is Hamiltonian switching for solid and liquid phases to get the $d^\Phi_G(c)$ coefficient in equation 57.

For solids, free energy of the reference Einstein Oscillator, $g^\Phi(c, T_0)$, is calculated at $T= 296K$ using Einstein temperatures equal to 315K and 275K for Mg and Li respectively.
Figure 5.3. Enthalpy per particle for Mg and Li during heating and cooling as a function of temperature.

as shown by equation 49. These temperatures are chosen for Mg and Li to reduce the variations in the switching integral and to improve the numerical precision. Samples are first cooled down to 0K at a volume corresponding to P=0 at T=296K to determine the equilibrium positions $r_{i0}$ of the Einstein crystal. Next, the average $⟨U - W_{\text{sol}}⟩$ is calculated at constant temperature and volume for $λ$ values between 0 and 1 at intervals of 0.05. Similar to enthalpy, these calculations are carried out in two steps, first $10^4$ steps to equilibrate the sample and next $10^4$ to calculate the thermodynamic ensemble average of $⟨U - W_{\text{sol}}⟩$. A sixth order polynomial fit calculates the integral shown in equation 49. Figure 5.4 shows the average $⟨U - W_{\text{sol}}⟩$ values for pure Mg and pure Li in the hcp and bcc phases respectively. At $λ \simeq 0$ values, non-interacting Einstein oscillators govern the dynamics. In this region, EAM Hamiltonian provides a small contribution to the interaction necessary to reach thermal equilibrium, and Einstein oscillators are not governed by isothermal thermostat. Therefore, long runs of 100 ps equilibration are done near $λ \simeq 0$ values.

For liquid phases, the integral $Δf_1$ and $Δf_2$ in equations 50 and 51 are calculated to determine the integral $gL(T_0)$ in equation 52. The free energy change $Δf_1$ in this case is evaluated at reference temperature 1200K. Similar to solid switching, the temperature
Figure 5.4. $\langle U - W_{sol} \rangle$ versus $\lambda$ for solid hcp Mg and bcc Li phase. $W$ is the reference system taken as Einstein oscillator with known free energy. $U$ is the CD-EAM Hamiltonian and $\lambda$ is the switching parameter between CD-EAM Hamiltonian and Einstein oscillator which varies between 0 and 1.

is chosen to reduce the variations in the switching integral and to improve the numerical precision. The first sample is equilibrated to get the volume at this temperature. The equilibrated sample is taken as the starting point for the switching process using a repulsive potential. Now, all the steps similar to solid switching are carried out to get the area of the integrand by sixth order polynomial fit as shown in figure 5.5.

Now, this liquid sample with repulsive potential is expanded to mimic an ideal gas at the constant temperature, $T_0$, by reducing the pressure from 125 kbar to 1 bar. Average pressure and density is obtained for $\lambda = 0$ corresponding to the ideal gas limit, $P=0$ and $\rho = 0$. This gives the evolution of pressure as a function of density, and the integral, $\Delta f_2$, in equation 50 is calculated as a sixth order polynomial fit to the curve shown in figure 5.6. This figure shows the adiabatic expansion of the liquid to reach the ideal gas.

The solid and liquid switching gives the coefficient $d_c$ in equation 56. Now, free energy as a function of temperature, $g_c^{(T)}$, for specific compositions is calculated. Figure 5.7 shows the representative $g_c^{(T)}$ curves for the pure Mg solid hcp phase and pure Li solid bcc phase.
Figure 5.5. $\langle U - W_{sol} \rangle$ versus $\lambda$ for liquid phase. See figure 5.4 for description of parameters.

Figure 5.6. Expansion and compression cycles for integral in equation 50 for Mg and Li gaseous phase.

together with liquid phases. The intersection of free energy of the solid hcp and bcc phases and the liquid phases give the melting point for pure elements. The solid and liquid Li free energy curves cross at 430 K, which is the thermodynamic melting point for pure Li EAM model used in the present work [12]. This melting point is 23K less than the experimental melting point of Li (453.6K). Similarly, Mg EAM potential [11] has a melting point of 960 K, which is 40K higher than the experimental value (921.8K). Both Sun et al. [11] and we
obtained 914+/-3 K as the melting temperature for the same pure Mg potential from the coexistence method [130]. This 4.6 % difference in melting point may be ascribed to the statistical error in determining the free energies of solid and liquid phases.

**Figure 5.7.** Free energy as a function of temperature, $g_c(T)$, for (a) pure Mg and (b) Li solid (hcp, bcc) and liquid phases.

Similar curves of $g_c(T)$ are obtained for different alloy compositions. A third order polynomial is again fit to coefficients $a_c^\Phi$, $b_c^\Phi$, $c_c^\Phi$, and $d_c^\Phi$ to get their variation as function of compositions $(a^\Phi(c), b^\Phi(c), c^\Phi(c),$ and $d^\Phi(c))$, which can be used in equation 57 to calculate $g^\Phi(c, T)$. Table 5.1 shows the values of third order polynomial coefficient fits.

Now, I calculate the free energy as a function of composition, $g^\Phi(c, T)$, for hcp, bcc, and liquid phases at different temperatures. Figure 5.8 shows an example functional at 400K and 800K. The common tangent construction of these phases is used to demarcate the phase boundaries and construct the phase diagram shown in figure 5.9. The CD-EAM potential reproduces the phase diagram well. At 300 K our phase diagram captures the following features: (1) Mg solid solution ($\alpha$) till 18 at. % Li, whereas the experiment shows maximum solubility of 17 at. % Li; (2) Li solid solution ($\beta$) phase is stable till 73 at. % Mg versus 65 at. % Mg solubility seen experimentally; (3) two phase region ($\alpha + \beta$) is stable from 18 to
Table 5.1. Third order polynomial fits to coefficients in equation 57 for (A) hcp phase, (B) bcc phase, and (C) liquid phase. These coefficients give meV/atoms unit for free energy when temperature is in Kelvin.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Cubic</th>
<th>Quadratic</th>
<th>Linear</th>
<th>Independent</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>-0.0147329</td>
<td>0.158114</td>
<td>-0.251253</td>
<td>-1.52542</td>
<td>0.9986</td>
</tr>
<tr>
<td>b</td>
<td>2.1443e-05</td>
<td>-2.53095e-05</td>
<td>1.74426e-05</td>
<td>0.000234831</td>
<td>0.20274</td>
</tr>
<tr>
<td>c</td>
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<td>-2.02442e-08</td>
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<td>0.7367</td>
</tr>
<tr>
<td>(d_G)</td>
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<tr>
<td>(B)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
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</tr>
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<td>1.40124e-06</td>
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<td>0.6123</td>
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<tr>
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<tr>
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</tr>
<tr>
<td>(C)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
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<tr>
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<td>0.000319774</td>
<td>0.2613</td>
</tr>
<tr>
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</tr>
<tr>
<td>(d_G)</td>
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<td>0.00260195</td>
<td>0.000606825</td>
<td>0.00185314</td>
<td>0.1704</td>
</tr>
</tbody>
</table>

27 at. % Li, whereas experiment shows from 17 to 30 at. % Li; (4) Eutectic melting point \([L \rightleftharpoons Mg(\alpha) + Li(\beta)]\) at 18 at. % Li and 900 K and experiment shows at 23 at. % Li and 861K; (5) however, CD-EAM potential is not able to capture the congruent melting point seen experimentally at 30 at. % Li.
Figure 5.8. $g^\Phi(c, T)$ at (a) 400K and (b) 800K for bcc, hcp, and liquid phases. The common tangent construction is used to derive the phase diagram.

Figure 5.9. Phase diagram from the present work compared with Saunders et al. [4]. $\alpha$ represents hcp phase, $\beta$ is bcc phase, $\alpha + \beta$ is two phase region, L is liquid region, and E represents eutectic point.
I presented here a rigorous calculation of the Mg-Li phase diagram from our model CD-EAM Hamiltonian. We believe that this is the first extensive atomistic simulation approach to calculate the Mg-Li phase diagram. Other researchers have used CD-EAM potential to successfully calculate the phase diagram for cubic systems such as Fe-Cu and Au-Ni [118, 126, 129]. The present calculations for Mg and Mg-Li alloys shows its application for non-cubic materials.

5.3. Lattice parameters and heat of mixing (HOM)

A 20x20x20 supercell and NPT ensemble is used to calculate the lattice parameter and HOM of the hcp and bcc phases. NPT ensemble equilibrates volume corresponding to zero externally applied pressure at the temperature of interest. The properties are calculated after equilibrating the samples. Lattice parameter for the bcc phase is calculated by measuring the distance between two atoms in [100] direction. For the hcp phase $a$ and $c$ lattice parameters are calculated by measuring the distance along [11\bar{2}0] and [0001] directions, respectively. The HOM for both phases is calculated as,

\begin{equation}
HOM = \frac{E_{Mg-Li} - XE_{Mg} - (1 - X)E_{Li}}{N}
\end{equation}

Where $E_{Mg-Li}$ is the total energy for Mg-Li alloy, $E_{Mg}$ and $E_{Li}$ are the cohesive energies for pure Mg and Li respectively, $X$ is the Li concentration, and $N$ is the number of atoms.

The variation of lattice parameters and $\Delta H^{mix}$ with Li concentration predicted by CD-EAM potential agree well with published literature values as shown in figure 5.10 and 5.11. The CD-EAM potential is able to reproduce both the $\langle a \rangle$ and $\langle c \rangle$ lattice parameters for the hcp phase, and thereby reproduces the $\frac{c}{a}$ ratio correctly. $\Delta H^{mix}$ for the hcp phase from simulation is lower than experimental values of Saunders [4] but matches well with a first principles study by Taylor et al. [18]. This could be because, during the fitting of the CD-EAM potential parameters, atoms are not allowed to move but when the potential is
relaxed in MD they are allowed to move thereby lowering the forces. On the other hand, $\Delta H^{\text{mix}}$ for the bcc phase matches well with experimental value.

5.4. Stacking fault energy

Stacking fault energy (SFE) variation with the composition will dictate how our newly created Mg-Li potential behaves when the hcp phase of the alloy is deformed plastically. Therefore, reproducing the correct trends for basal and prismatic SFE is important. The SFE is calculated as the difference between the energy of the system with stable stacking fault ($E_{SF}$) and the perfect system ($E_{\text{perfect}}$) as shown in equation 59.

\[
SFE = \frac{(E_{SF} - E_{\text{perfect}})}{A}
\]

Here, $A$ is the area of the stacking fault surface.
The stable SFE is calculated using the methodology given by Yasi et al. [123] who also used the same Mg potential as this work. Our calculations for both basal and prismatic SFE of pure Mg agree with their results. A stable stacking fault is observed on the basal slip system (0001) [1\(\bar{1}\)00] and prismatic slip system (1\(\bar{1}\)00) [1\(\bar{1}\)21]. The (1\(\bar{1}\)00) [1\(\bar{1}\)20] prismatic stacking fault is not stable for pure Mg EAM potential and Mg-Li CD-EAM potential. Details about the stable prismatic plane slip system for pure Mg are mentioned by Yasi et al. [123], and the addition of Li does not change this trend. The variation of SFE with Li atom % is shown in figure 5.12. In the present study, basal SFE increases by 90 % whereas prismatic SFE increases slightly by 4% when 10 atomic % Li is added. The literature has reported varying effects on SFE with Li addition[31, 19, 20, 17]. An experimental study by Agnew et al. [31] suggested that the basal SFE may increase with Li addition and non-basal SFE may decrease with Li addition, but they have not reported any quantitative values of SFE. The MEAM potential by Kim et al. [17] showed a decrease in basal and prismatic
SFE by 10 % when 10% Li is added. On the other hand, recent first principles studies \cite{19, 20} have shown that basal SFE increases with Li addition which correlates well with our result. These first principles studies have reported SFE values for a single alloy composition, which is insufficient to determine a trend. Furthermore, they do not report any data for the prismatic SFE.

To verify the qualitative nature of basal and prismatic stacking fault energy trends, I carried out density functional theory (DFT) calculations of these planar defects using four random configurations at each alloy composition to determine the average SFE. These calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) \cite{111}. The cutoff energy used for the plane wave basis set is 400 eV. The Generalized Gradient Approximation with electron exchange-correlation described by Perdew-Burke-Ernzerhof parameterization \cite{82} is used to calculate the SFE. The energy cutoff for the relaxation is $10^{-5}$
Brillouin zone sampling is done using the Methfessel-Paxton smearing method with the width 0.2 eV, and the K-points meshing is $9 \times 9 \times 1$ on a Γ centered grid. A $2 \times 2 \times 13$ and $2 \times 13 \times 2$ supercell is used for basal and prismatic plane SFE calculation respectively, for a total of 104 atoms. A stable SFE for the basal plane is observed on (0001) [1100] slip system for pure Mg and Mg-Li alloys, and the SFE increases with addition of Li in Mg. A stable stacking fault structure is not observed for the prismatic slip system from DFT calculations on (1100) [1120] and (1100) [1121] slip system. Therefore, here I report the unstable SFE for the prismatic plane. The unstable SFE for the prismatic plane increases by 4% with the addition of 10 at. % Li. Thus, results of SFE from the present DFT calculations match qualitatively with our newly developed CD-EAM potential and are shown in figure 5.12. The mismatch in magnitudes of prismatic SFE arises due to the dependency on SFE properties of the pure Mg EAM potential. Developing a more faithful EAM Mg potential is beyond the scope of this work. The important point to note here is that the CD-EAM potential is able to differentiate satisfactorily between the relative magnitudes of prismatic and basal SFE. Local charge distribution and bonding calculations from DFT methodology can help understand the increase or decrease in the SFE on different slip systems and can be further used to verify the correct trends with Li addition. It can help resolve the different qualitative nature of SFE with Li addition from present CD-EAM potential and Kim et al. [17] MEAM potential. I propose these calculations in the future work section of this dissertation.

SFE indicates the amount of dissociation of stacking faults- higher the SFE lower the dissociation width and vice-versa. The increase in basal SFE indicates decrease in dissociation width of basal dislocation with Li addition. Indeed, Agnew et al. [31] observed basal stacking faults in pure Mg but not in Mg-Li alloys in transmission electron microscopy studies. This experimental evidence is in agreement with the present result that addition of Li increases the basal SFE.
5.5. Bulk modulus

Bulk modulus \((B)\) is the resistance of a material to volume deformation and is calculated as the ratio of infinitesimal change in pressure \((dP)\) with relative change in volume \((dV)\).

\[
B = -V \frac{dP}{dV}
\]

Figure 5.13. Bulk modulus at 0K (a) hcp (b) bcc phase from present simulation compared with experimental data [21, 22, 23, 24], first principles calculations [25, 26, 27], and atomistic simulations [17]

Bulk modulus variation for the hcp and bcc phases from CD-EAM potential is shown in figure 5.13. The bulk modulus for the hcp phase from reference [21] is calculated by using the relation \(B = \frac{2}{3}(C_{11} + C_{12} + 2C_{13} + C_{33}/2)\). For the hcp phase, the experimental values decrease by 7% with the addition of 16% Li, whereas the CD-EAM potential shows a slight increase of 6% when 16% Li is added. The maximum deviation for the hcp phase bulk modulus is 15% at 16% Li when compared with the literature. For the bcc phase the values agree qualitatively with literature. The maximum deviation observed for the bcc phase bulk modulus value is 30 % at 40% Li.
The bulk modulus variation from CD-EAM potential for both phases deviates from the literature values. In several versions of the potentials I generated, it is found that improving the bulk modulus trend detrimentally shifted the phase boundaries on the calculated phase diagram. Therefore, the scale of deviation in the bulk modulus trend is qualitatively acceptable, and this version represented an acceptable compromise.

5.6. Energy for hcp to bcc transformation

The barrier to transform the hcp phase into the bcc phase during deformation is given by energy for the hcp to bcc transformation. For the present CD-EAM potential, I calculated this barrier ($\Delta E_{hcp-bcc}$) as,

\[
\Delta E_{hcp-bcc} = \frac{(E_{hcp} - E_{bcc})}{N}
\]

Where, $E_{hcp}$ and $E_{bcc}$ are the total energy of the structures with equilibrium hcp phase and bcc phase, respectively.

Figure 5.14 compares the hcp to bcc transformation energy as a function Li addition from CD-EAM potential with DFT values calculated by us. The transformation energy from the CD-EAM potential is lower compared to DFT values for pure Mg and Mg-Li alloys. Although, the potential prediction is qualitatively similar to DFT and the qualitative disagreement between two methods arises from the pure Mg potential.

5.7. Conclusions

The reliability and transferability of our Mg-Li CD-EAM potential was tested in this chapter. Figure 5.15 summarizes the inputs and targets used in the fitting and properties predicted by our CD-EAM potential. This alloy potential satisfactorily reproduces the experimental phase diagram and variations in lattice constants, heat of mixing, and stacking fault energy (SFE) as a function of Li concentration. The important property for mechanical deformation studies is the SFE, and this potential reproduces qualitatively correct basal SFE as shown by first principles calculations and suggested by experiments.
Figure 5.14. hcp to bcc transformation energy from CD-EAM potential compared with DFT values calculated as a part of present work. The qualitative trends from CD-EAM and DFT match for Mg-Li potential, although the discrepancy in quantitative values originate from pure Mg potential used in the fitting procedure.

<table>
<thead>
<tr>
<th>Inputs for the Potential</th>
<th>Target Used</th>
<th>Properties Reproduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg EAM Potential*</td>
<td>Heat of Mixing</td>
<td>Lattice Constant</td>
</tr>
<tr>
<td>Li EAM Potential*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lattice Constants- bcc &amp; hcp phase</td>
<td></td>
<td>Bulk Moduli</td>
</tr>
<tr>
<td></td>
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</table>

Figure 5.15. Figure shows the summary of input and target parameters and properties reproduced by the Mg-Li CD-EAM potential. *Note that single component Mg and Li potentials used different properties like lattice constants, vacancy formation energy, bulk modulus, elastic constants, and stacking fault energy in fitting.
There is scope to improve values of bulk modulus, hcp to bcc transformation energy, and remedy the absence of pyramidal type II slip system in our potential. We believe that these shortcomings come from the pure Mg potential used in the fitting procedure and its modification is beyond the scope of the present work. However, these shortcomings do not affect our conclusions for deformation studies in the next chapters.

In comparison to the other Mg Li potential in the literature [17], CD-EAM potential present important advantages such as a creating a faithful phase diagram and predicting correct trends in the compositional dependence of the basal and prismatic stacking fault energies at a small computational cost. All these are important ingredients of a transferable interatomic potential necessary for reliable prediction of deformation behavior.
6.1. Introduction

The lightest weight and high specific strength multicomponent Mg-Li-X-X-X alloys (where, X=Al, Zn or Zr) are promising candidates for many applications if we can overcome their low formability at room temperature, large creep at relatively low stresses, and oxidation problems [29, 51]. A fundamental understanding of deformation mechanisms in simple binary Mg-Li alloys, that are still largely unknown, can guide us in developing stable and strong Mg-Li-X-X-X alloys. Therefore, I study the strength and deformation mechanisms in randomly oriented nanocrystalline (NC) hcp Mg-Li alloys using atomistic simulations. Such simulations have been used extensively in the past two decades to study defect mechanisms such as dislocation nucleation and interaction, twin formation, grain boundary sliding, and existence of Hall-Petch type behaviour mostly in bulk and NC fcc materials [131, 132, 39, 35, 133, 40, 42]. Such study of deformation in more complex and industrially relevant hcp materials by MD simulation is relatively scarce [45, 46, 134, 43, 44]. For example, Zheng et al. [43] discuss the nucleation of basal partial and extended dislocations, non-prevalent twinning systems, and an allotropic transformations from the hcp to fcc crystal structure in Co. They do not discuss the presence of non-basal slip systems (prismatic and pyramidal). In addition, the rare observance of twins in these low stacking fault energy (SFE) systems is surprising. Kim et al. [45, 46] discuss the existence of basal and non-basal slip systems and twinning systems in the preferentially oriented columnar 2-D geometry in NC Mg during creep. Kim [47] also studied the effect of grain size on deformation in randomly oriented 3-D NC Mg while Pozuelo [48] et al. investigated how twins influence deformation in Mg-Al alloys. The present molecular dynamics (MD) simulations in randomly oriented NC Mg-Li alloys can advance the understanding of deformation mechanisms in the hcp alloys.
In this chapter, I will use the newly created CD-EAM potential to understand the effect of Li addition on the deformation mechanisms of NC hexagonal close packed (α) Mg-Li alloys. Understanding the atomic mechanisms for the Li addition in NC Mg can provide useful insights that enhance the literature knowledge of this important material system.

Pure Mg is anisotropic because of the presence of only one active basal ⟨a⟩ slip system at room temperature. The ⟨a⟩ slip alone cannot accommodate the deformations along ⟨c⟩ direction. Furthermore, the presence of less than five active slip systems does not satisfy the Von-Mises criterion [57] and can lead to failure due to non-homogeneous deformations. Therefore, pure Mg has low ductility and formability. Three main methods are proposed to improve the ductility of Mg [33],

1. Grain refinement by severe plastic deformation or conventional dynamic recrystallization.
2. Texture modification in the conventional sheet material.
3. Adding alloying elements such as Li.

These methods improve ductility by reducing the plastic anisotropy between basal and non-basal slip systems. A schematic diagram in figure 6.1 illustrates this reduction with reducing the grain size or adding alloying elements.

In the present work I will investigate the effect of Li alloying on the ductility enhancement and plastic anisotropy. Such alloying also decreases the ductile-brittle transition to below liquid nitrogen temperature [50, 33]. Figure 6.1 shows the large plastic anisotropy between basal and non-basal slip modes for the bulk hcp systems. Basal slip is dominant at coarser grain sizes and a high plastic anisotropy is also observed because the nucleation stress for non-basal slip modes is ~10^2 higher than the basal mode. Nanometer grain sizes [28] and alloying elements reduce this plastic anisotropy factor to about two and triggers all the slip systems.
Figure 6.1. Schematic diagram showing the magnitude of anisotropy in the nucleation stress of basal and non-basal slip systems ($\tau_{\text{nucleation}}$) in the hcp systems [28]. The anisotropy decreases when grain size ($d$) is reduced to nanoscale or via alloying.

6.2. Simulation Methodology

In this section, I present the methodology of MD simulations of uniaxial compression deformations for 3D randomly oriented grains of NC hcp Mg and Mg-Li alloys. Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), a classical molecular dynamics (MD) code is used for simulations [110]. Common neighbor analysis (CNA) is used to identify the local crystal structure of atoms such as fcc, hcp, non-basal slip system, or grain boundary atoms [109]. OVITO software is used for visualizing simulation snapshots after removing thermal noise via short minimization to highlight crystal defects [112].

The NC Mg system, with randomly oriented grains and random grain boundaries, used in the present MD simulations is shown schematically in figure 6.2. There are 11 grains
Figure 6.2. (a) Nanocrystalline (NC) geometry used for Mg-0%Li system is shown. There are 11 grains in the NC system. Atoms are colored by the number identity of the grain they belong to. Arrows show the compression direction. (b) Figure shows grain size distribution in the NC sample with average grain size being 12.91 nm in diameter.

in the NC sample with average grain size of 12.91 nm in diameter. Grain size is calculated by multiplying the number of atoms in each grain with atomic volume. The NC simulation cell is 231x248x234 Å$^3$ and has 580964 atoms. Periodic boundary conditions are used in all directions. After creating the NC system, I delete grain boundary atoms separated by less than 1.5Å because they have unphysical, high-energy values. The NC is then annealed at 300K for 100ps using the time step $\Delta t=1$ fs. Berendsen barostat is used to control the pressure and temperature of atoms is maintained at 300K by explicitly rescaling the velocities of the atoms. The equilibration at 300K allowed the intergranular stresses to reduce to less than 10MPa and rearrangement of atoms at grain boundaries. For Mg-Li alloys, Li atoms replace randomly selected Mg atoms and the structure is annealed at 300K to reduce the intergranular stresses. I present the results for Mg-10%Li system in this work. Figure 6.3 shows the representative NC sample used for Mg-10%Li system.

Uniaxial compression is applied to NC in Z direction at a strain rate of $10^8$ s$^{-1}$ and constant temperature of 300K. Uniaxial compression testing along X and Y directions
Figure 6.3. NC sample used for Mg-10%Li composition. This figure shows the distribution of Li atoms in Mg-10%Li composition, grains are not shown here. Refer figure 6.2 for the distribution of grains. Red and Blue atoms represent Mg and Li, respectively. This composition is generated by randomly substituting 10% of Mg atoms in the NC with Li atoms.

give qualitatively similar results as along Z direction, which suggests that the random grain boundaries for 11 grains produces a population of grain boundary orientations large enough to address the Li addition effects on deformation mechanisms. I used three different configurations of random distributions of Li atoms for each compression simulation. The deformation mechanisms for these different configurations of loading directions and random distributions of Li atoms are similar and the yield strength values are within 1% of the average values. Therefore, I only discuss results for a representative Mg-10%Li system. I also quantify the yield strength variation as a function of Li composition and identify the related underlying mechanism. Kim et al. [45, 46] observed intergranular cracking for the same EAM Mg potential [11] under tension at low plastic strains (< 3%) because of the low twinning and pyramidal \(\langle c + a \rangle\) slip. So, to avoid intergranular cracking, I study the deformation mechanisms under compression instead of tension. The influence of grain size, number of grains, and strain rate on deformation is not the subject of this study, which uses
a NC sample as a way to sample a large diversity of stress states that likely display most of the unit mechanisms of plasticity in Mg-Li alloys.

6.3. Signatures of defect processes in hcp NC Mg and Mg-Li alloys

Figure 6.4 illustrates slip systems available in hcp metals. In contrast to the five independent slip systems available in cubic crystal structure, the hcp systems have basal \{0001\}, prismatic \{10\overline{1}0\}, and pyramidal \{10\overline{1}1\} or \{11\overline{2}2\} slip planes with Burgers vectors along either \langle a \rangle \langle 11\overline{2}0 \rangle or \langle c + a \rangle \langle 11\overline{2}3 \rangle directions. While \langle a \rangle type basal slip is dominant in Mg, slip also occurs on prismatic and pyramidal planes at high temperature or at high intergranular stresses in polycrystalline materials.

The \langle a \rangle type slip provides only four independent slip systems (2 basal and 2 prismatic) and does not satisfy the von Mises criterion for homogeneous deformation of polycrystalline materials. It also fails to provide deformation along the \langle c \rangle direction. The deformation along the \langle c \rangle direction of the hcp metals is enabled by pyramidal \langle c + a \rangle slip and via three twinning modes shown in figure 6.4(b). For example, an additional twinning mode is observed in the hcp Mg at room temperature [135] while pyramidal \langle c + a \rangle dislocations are known to nucleate at high temperature or high intergranular stresses. Addition of Li is also known to activate pyramidal slip system and increases the ductility [6, 50].

Figure 6.5 summarizes the slip systems according to the Burgers vector \langle a \rangle, \langle c \rangle, and \langle c + a \rangle in hcp crystals. Also, the slip systems which show stable stacking fault are observed in the present simulations and marked as Yes. Note that slip systems marked with No are full dislocations and do not show stable stacking fault [49, 123, 136] but may be present in the NC samples. CNA identifies these full dislocations as disordered atoms and it is difficult to separate a full dislocation from other defects that are also identified as disordered type atoms (grain boundaries, twin boundaries, and pyramidal type I dislocations) and are therefore not observed in the present NC deformation simulations. Presence of five independent deformation modes that include basal, pyramidal, and three twins in the NC simulations with our CD-EAM Mg-Li potential fulfils the Von Mises criterion for homogeneous deformation in polycrystalline materials. I will now summarize the signatures of individual modes before
Figure 6.4. Slip systems in the hcp metals are shown. (a) Basal plane \{0001\} \langle 11\bar{2}0 \rangle, Prismatic plane \{10\bar{1}0\} \langle 1\bar{1}20 \rangle, Pyramidal plane type I \{10\bar{1}1\} \langle 1\bar{1}23 \rangle and type II \{1\bar{1}22\} \langle 1\bar{1}23 \rangle slip systems (b) tension twinning (TTW) \{10\bar{1}2\} \langle 1\bar{1}21 \rangle, compression twinning (CTW1) \{10\bar{1}3\} \langle 30\bar{3}2 \rangle and compression twinning (CTW2) \{10\bar{1}1\} \langle 1\bar{1}2 \rangle.

6.3.1. Basal dislocations

CNA is used to characterize the hcp and fcc type atoms in the system. Atoms in the core of basal dislocations in hcp metals have ABC stacking of the fcc crystals. In figure 6.6, hcp and fcc atoms are coloured red and green, respectively. Basal dislocation dissociates into two partials and the dissociation reaction is given as [54], \frac{1}{3}[2\bar{1}10] = \frac{1}{3}[1\bar{1}00] + \frac{1}{3}[10\bar{1}0].

The Intrinsic I2 (ABABCABA) stacking fault is bounded by \frac{1}{3}[1\bar{1}00] partial dislocation and is shown by two-layers of fcc atoms in figure 6.6. The intrinsic I1 fault, with ABABACABA stacking, is bounded by \frac{2}{3}[1\bar{1}00] partial dislocations and has two layers of the fcc atoms. In addition, extended basal dislocations are also observed.
6.3.2. Pyramidal type I dislocations

The proposed dissociation for \{10\overline{1}1\} \langle 11\overline{2}3\rangle pyramidal type I slip system is summarized in Table 6.1. The dislocation splits into two or three partials. This splitting depends on where a minimum is obtained on the Generalised stacking fault energy (GSFE) curve for the particular interatomic potential used in the simulations. But, recent MD simulations studies that used the same Mg EAM potential [121] show different dissociation reactions
Figure 6.6. A basal I2 stacking fault is shown here. Atoms are colored by CNA with red and green representing hcp and fcc type atoms, respectively. X and Y are two partials $\frac{1}{3}[1\bar{1}00]$ and $\frac{1}{3}[10\bar{1}0]$ respectively.

Table 6.1. Summary of dissociation reactions for pyramidal type I dislocation in hcp Mg.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Dissociation reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stohr and Porrier [137]</td>
<td>$\frac{1}{3}[1\bar{1}23] = \frac{1}{6}[20\bar{2}3] + \frac{1}{6}[02\bar{2}3]$</td>
</tr>
<tr>
<td>Bacon and Liang [138]</td>
<td>$\frac{1}{3}[\bar{1}1\bar{2}3] = \frac{1}{4}[1012] + \frac{1}{12}[1432] + \frac{1}{6}[\bar{1}012]$</td>
</tr>
<tr>
<td>Ando et al. [139]</td>
<td>$\frac{1}{3}[1\bar{1}23] = [0001] + \frac{1}{3}[10\bar{1}0] + \frac{1}{3}[01\bar{1}0]$</td>
</tr>
<tr>
<td>Li and Ma [140]</td>
<td>$\frac{1}{3}[1\bar{1}23] = \frac{1}{2}[01\bar{1}2] + \frac{1}{6}[2\bar{1}\bar{1}0]$</td>
</tr>
<tr>
<td>Kim et al. [46]</td>
<td>$\frac{1}{3}[\bar{1}\bar{1}23] = \frac{1}{6}[1013] + \frac{1}{18}[2643] + \frac{1}{6}[2023]$</td>
</tr>
</tbody>
</table>

[45, 140]. Experiments have indicated the presence of $\langle c+a \rangle$ dislocation on pyramidal type I plane [5] but have not proposed a dislocation dissociation reaction [140].

To characterize the above mentioned dissociation reaction, I calculate the 2D GSFE curve for pyramidal type I slip system $\{10\bar{1}1\} \langle 11\bar{2}3 \rangle$. Nogaret et al. [136] calculated GSFE curves but did not discuss the dissociation reaction. I use their approach to calculate the $\{10\bar{1}1\} \langle 11\bar{2}3 \rangle$ GSFE curves shown in figure 6.7(a). $\langle 1\bar{1}02 \rangle$ and $\langle 11\bar{2}0 \rangle$ directions lie on this
Figure 6.7. (a) A 2D contour plot of SFE for the pyramidal-I dislocation with stacking faults F1 and F2 are shown. The stable SFE for F2 fault is over twice the F1 energy and we do not see F2 in NC simulations (b) Local atomic structure on the pyramidal plane is shown with the \( \langle c+a \rangle \) vector marked. Arrows show the displacement needed for fault F1. (c) Atomic structure of the F1 fault after displacements. Light blue atoms lie on the bottom and dark blue atoms are on the top planes.

The \( \langle c+a \rangle \) \langle 11\bar{2}3 \rangle \) direction is along the points joining the start and end of the rectangle shown in the figure. There are two minima F1 and F3, respectively, along the \( \langle 1\bar{1}02 \rangle \) direction on GSFE curve there at \( \frac{1}{4} \langle 1\bar{1}02 \rangle \) and \( \frac{1}{8} \langle 1\bar{1}02 \rangle \), which suggests that there are two stable stacking faults on this plane. The third fault at F2 \( \frac{1}{12} \langle 1432 \rangle \) joining these minima completes the full \( \frac{1}{3} \langle 11\bar{2}3 \rangle \) pyramidal \( \langle c+a \rangle \) vector. So, the dissociation reaction can be written as,
Figure 6.8. Summary of the steps followed to identify the pyramidal type I stacking faults in the NC deformations. (a) Atomic structure of the pyramidal type I fault F1 after displacements. Distorted orange hexagon shows the stacking perpendicular to the fault F1. This exercise is used to find F1 fault structure in NC samples. (b) A slice of the NC sample. Red atoms are hcp type, grey atoms are either grain boundary type or pyramidal dislocations type. The two vertical black lines indicate an ordered stacking protruding from grain boundaries. A magnified view of this figure is shown in figure (c). Figure (d) shows a magnified view along the two horizontal lines. Finally, the structure in perpendicular direction to (d) along the black arrow is shown in figure (e). The orange hexagonal structure and \( \langle c + a \rangle \) length matches with the structure shown in (a). The structure in figure (e) identifies F1 fault in the NC samples.
\[
\frac{1}{4}[\overline{1}012] + \frac{1}{12}[1432] + \frac{1}{6}[\overline{1}012] \rightarrow \frac{1}{3}[\overline{1}123]
\]

This dissociation is in agreement with Liang and Bacon [138]. The atomic structure perpendicular to the \{10\overline{1}1\} plane is shown in figure 6.7(b). The two layers of atoms are shown and colored as per the position perpendicular to \{10\overline{1}1\} plane. Dark blue atoms represent layer on top and light blue atoms are on bottom plane. The fault F1 and F2, with \frac{1}{6}[10\overline{1}2] and \frac{1}{4}[10\overline{1}2] fault vectors respectively, are along the \langle c \rangle direction, and \frac{1}{12}[1432] vector is along \langle c + a \rangle direction complete the dissociation reaction. I observe fault F1 with magnitude \frac{1}{6}[10\overline{1}2] in the NC simulations as this has lowest unstable barrier to nucleate. The stable structure of \frac{1}{6}[10\overline{1}2] SF is shown in figure 6.7(c) after displacement of the atoms.

The steps followed to identify of pyramidal type I fault F1 in NC deformation simulations are shown in figure 6.8.

6.3.3. Twins

**Figure 6.9.** Figure shows the twinning systems observed in the hcp NC simulations. Red, green, and grey colors represent hcp, fcc, and twin boundary region atoms. The black lines indicate the basal plane \langle a \rangle \langle 1\overline{1}20 \rangle directions for the hcp regions across the twin boundary. (a) \{10\overline{1}2\} \langle 10\overline{1}1 \rangle tension twinning with 86° angle (b) \{10\overline{1}3\} \langle 30\overline{3}2 \rangle compressive twinning with 64° angle (c) \{10\overline{1}1\} \langle 1\overline{1}02 \rangle compression twinning with 56° angle.

The approach of Barrett et al. [59] is used to identify the twins. First, I identify the basal plane across the twin boundaries and then calculate the misorientation angle between the two mirror planes along \langle 1\overline{1}20 \rangle or \langle 1\overline{1}00 \rangle direction to characterize the twin systems.
Three twinning systems are identified in NC simulations and are shown in figure 6.9 with their misorientation angles. The black lines in this figure indicate the direction $⟨a⟩\langle 11\bar{2}0⟩$ in basal plane for the hcp regions across the twin boundary. The angle between two $⟨a⟩$ directions specifies the particular type of twin. A $\{10\bar{1}2\} \langle 10\bar{1}1⟩$ tension twin has 86 degrees misorientation angle and is observed frequently in the simulations. Whereas, the two compression twinning systems (i) $\{10\bar{1}3\} \langle 30\bar{3}2⟩$ with 64 and (ii) $\{10\bar{1}1\} \langle 10\bar{1}2⟩$ with 56 degrees angles, respectively, are observed at high strains but less frequently. Hereafter, I refer $\{10\bar{1}2\}$ tension twinning as TTW, $\{10\bar{1}3\}$ compression twinning as CTW1, and $\{10\bar{1}1\}$ compression twinning as CTW2.

Having established the signatures of important defects in the hcp systems, I now present deformation in NC Mg-Li as a function of strain.

6.4. Overall Mechanical behavior of pure Mg and Mg-Li alloys

The compressive stress-strain plots of pure Mg and Mg-10%Li alloy at 300K are shown in figure 6.10. The stress in this graph is the Von Mises stress ($\sigma_{VM}$) defined as,

$$\sigma_{VM} = \sqrt{\frac{1}{2} [(\sigma_{xx} - \sigma_{yy})^2 + (\sigma_{yy} - \sigma_{zz})^2 + (\sigma_{zz} - \sigma_{xx})^2] + 3(\tau_{xy}^2 + \tau_{yz}^2 + \tau_{zx}^2)}$$

Here, $X, Y,$ and $Z$ are the coordinate directions. $\sigma$ is the uniaxial stress and $\tau$ is the shear stress.

First, the maximum stress point on this graph is taken as the yield strength ($Y$). Strains at which different deformation modes nucleate are marked on this graph. Pure Mg yields at 0.91 GPa while Mg-10%Li NC yields 0.77 GPa indicating that the yield strength ($Y$) decreases with the Li addition. The 14.5% decrease in yield strength suggests that the Li addition affects the energetics of Mg-Li NC alloys in a manner that softens the NC samples. This is indicative of solid solution softening in Mg-Li alloys. The interplay between the strength and ductility suggests that the decrease in strength implies an increase in ductility with the Li addition.
Figure 6.10. Compressive stress-strain response of the pure Mg and Mg-10%Li alloy at 300K uniaxially loaded along Z direction. The yield strength (Y) decreases with addition of Li in Mg. Nucleation sites for various deformation modes are also marked.

This solid solution softening in the our simulations qualitatively matches the previous experimental observation of decrease in strength in Mg-15 at.% Li alloy by Yoshinaga et al. [5] and decrease in flow stress in Mg-5 wt.%Li alloy by Agnew et al. [6]. These two studies attribute the observed decrease in strength in Mg-Li alloys to increased non-basal \((c + a)\) deformation processes.

The stress-strain graphs in figure 6.10 show the same qualitative response for Mg-0 at.%Li and Mg-10 at.%Li compositions. Three distinct deformation stages are evident as,

1. A linear elastic stress-strain region up to 2.75% strain. The NC sample is elastic in this region and no defects nucleate in the bulk grains.
(2) Region with reduced hardening that extends up to 5% strain for pure Mg and up to 3.5% strain for Mg-10%Li. Defects nucleate in this region and the maximum strength point or yield strength point (Y) is observed here.

(3) Region with decreasing stress wherein twins nucleate and complex dislocation interaction processes occur.

The nucleation of different defects is marked at the corresponding strain % on the plots for both compositions. I will discuss these atomic deformation mechanisms in the next section.

6.5. Deformation mechanisms of pure Mg and Mg-Li alloys

In this section, I will discuss the microstructure evolution with increase in strain. These defect processes were marked earlier in figure 6.10.

Figures 6.11 and 6.12 show the microstructure evolution for Mg-0 at.%Li (left) and Mg-10 at.%Li (right) at increasing strains. Microstructures are analyzed by taking multiple slices in the NC sample. Slices are taken at the same location for both compositions and are shown to highlight and compare the deformation mechanisms. I will specify if similar or dissimilar deformation modes are present elsewhere in the sample. Atoms are colored according to the CNA with red, green, and grey atoms, respectively, identifying hcp, fcc (basal stacking fault), and disordered atoms (grain boundary, pyramidal stacking fault or twin boundary atoms). The capital letters represent different deformation modes. A is for basal stacking fault, B for pyramidal, C for TTW, D for CTW1 and E represents CTW2 modes. The smaller figures in the column on the extreme right show the magnified view of deformation mode in the regions marked by circle or ellipse. Arrows in the figure 6.12 show the direction of propagation of twinned regions and boundaries. Shaded areas blue, green, and yellow show the TTW, CTW1, and CTW1 twinned grain areas respectively.

The stress-strain curve for NC sample shows linear behavior until 2.75% strain when basal dislocations first nucleate as shown in figure 6.11(a-b). Basal dislocations are the only deformation mode present for both Mg-0%Li and Mg-10%Li at this strain. The stress-strain graph shows a non-linear behavior after this point until yield strength is achieved. The dislocation nucleation below yield strength point is triggered by high intergranular stresses.
The deformation mechanisms in NC Mg (left column) and Mg-10%Li (right column) are shown as a function of strains. Atoms are colored according to CNA. Red denotes hcp, green is fcc type, and grey denotes disordered atoms either grain boundary, pyramidal dislocation cores, or twin boundaries. A is the basal stacking fault, B is pyramidal type I dislocation, C is TTW, D is CTW1, and E is CTW2. Blue, green, and yellow shaded areas are the twinned regions TTW, CTW1, and CTW2, respectively. Inset shows the close up view of the deformation mode in consideration. (a-b) At 2.75% strain, shows basal partial dislocation nucleation (c-d) at 3% strain.

at grain boundaries. Basal dislocation regions circled in figure 6.11(a-b) are smaller for Mg-10%Li. Whereas, Mg-0%Li show higher basal dislocation activity. Similar relative amount of basal dislocation activity is seen in the entire 3D samples of Mg-0%Li and Mg-10%Li. The elastic strain of \(-2.75\%\) required to nucleate dislocations matches a previous study of
Mg using columnar NC, and it is about one order of magnitude larger than the experimental values. The higher elastic strains likely result from high strain rates, and small grain sizes in the present MD simulations.

Pyramidal dislocations nucleate in both Mg-0%Li and Mg-10%Li systems at higher strains. Pyramidal type I stacking faults (B) are shown in figure 6.11(c-d) at 3% strain. Note the larger area of pyramidal dislocation activity in marked region of the Mg-10%Li system. Higher activity of pyramidal dislocations is also observed in the entire sample of Mg-10%Li, indicating solid solution softening for pyramidal dislocations with the addition of Li. Thus, in the early stages of plasticity (< 3% strain), basal and pyramidal type I dislocation nucleation dominate and grain boundaries act as nucleation sites for these deformation modes.

When deformation increases to 4.75% strain, TTW nucleates at the intersection of grain boundaries and pyramidal dislocations as shown in figure 6.12(a-b). Yield strength is reached with the nucleation of TTW and stress drops after this point for both compositions. The TTW activity in Mg-10%Li is larger than Mg-0%Li as indicated by the presence of two TTW in the former compared to one in the latter. TTW propagates larger distances in Mg-10%Li, as shown by larger arrows and bigger shaded area. The same trend is observed throughout the sample indicating that addition of Li favors the nucleation and propagation of TTW.

At high strains (> 5.5%), CTW1 is observed. Figure 6.12(c-d) shows the nucleation of \{10\bar{1}3\} CTW1 at 6% strain from the grain boundary of tensile twinned (TTW) grain. Thus, TTW likely aids the nucleation of CTW1. As shown by the arrows in this figure, CTW1 has propagated less distance in Mg-10%Li. At this high strain level, basal slip and TTW activity is also pronounced. As seen in these figures, Mg-10%Li shows less basal stacking fault area and propagation as compared to Mg-0%Li. TTW nucleates in two grains in Mg-10%Li whereas only in one grain in Mg-0%Li and a similar pattern is seen in the entire NC sample. These observations strengthen the previous conclusion that Li addition hardens basal slip but softens TTW mode.
Figure 6.12. Refer to figure 6.11 for description of features and color coding scheme. The arrow indicates the propagation direction of the twinned region and boundary for a specific twin. In this figure (e-f) are at 4.75% strain. TTW nucleation from pyramidal-I dislocation is shown. (g-h) are at 6% strain and shows the CTW1 nucleation inside the grain from tension twinning. (i-j) are at 6.75% strain and shows the CTW2 nucleation from tension twinning.
The Li addition hardens CTW2. Figure 6.12(e) shows that \{10\overline{1}1\} CTW2 nucleate inside a grain in Mg-0%Li from TTW at 6.75% strain. For Mg-10%Li, figure 6.12(f) shows that the CTW2 activity in Mg-10%Li is suppressed because the TTW boundary is thicker and it propagates faster than in Mg-0%Li. Less basal and more TTW activity is also seen in Mg-10%Li alloys as shown in figure 6.12(e-f).

It is now clear that the presence of TTW, CTW1, and CTW2 at high strains and high plasticity regions provides the additional deformation mechanisms. If the initial 2.75% elastic strain is subtracted, the nucleation of TTW at low plastic strains (\(\sim 2.25\%\)) from the grain boundaries and CTW1 or CTW2 nucleation at high strains (\(\sim 3.75\%\)) inside the grains or at grain boundaries matches the previous study of columnar Mg NC by Kim et al. [45] as well as many experiments [141, 142, 143, 144, 145]. At high strains (> 5.5%), transformation of some atoms in the hcp and twin boundary regions of NC samples to the distorted bcc phase is observed because the hcp to bcc transformation energy is low for the Mg potential used in this study compared to literature values (\(\sim 50\%\) lower) [11]. We calculated the variation of transformation energy with Li addition- 10% Li addition lowers this energy by 60%. These transformations are not discussed here as it happens at high strains (> 5.5%) strain and is beyond the scope of the present work.

6.6. Relative activity and reduction of plastic anisotropy

The previous section describes the activity of each deformation mode qualitatively. Here I quantify the activity of each deformation mode to make a distinction between them. I quantify the contribution of each deformation mode to the total plasticity by calculating the fraction of individual deformation modes, the so-called relative activity \(R\), defined as [6],

\[
R = \frac{\text{Atoms(One deformation mode)}}{\text{Atoms(All deformation modes)}}
\]

Where the numerator is the number of atoms in an individual deformation mode such as basal, pyramidal dislocations, TTW, or CTW, and the denominator is total number of atoms in all deformation modes. The numbers of atoms in each deformation mode are
calculated by counting the total atoms in a specific deformation mode. For the basal stacking fault, I counted the total number of fcc atoms identified by the CNA. For pyramidal dislocations, since CNA identifies pyramidal and grain boundary atoms as disordered, I first identified the pyramidal stacking fault area and then counted the number of atoms. For twins, I counted the number of the hcp atoms in the twinned area for the twinning mode under consideration.

The comparison of $R$ calculated at same strain values will help determine the dominant deformation mode in Mg-0%Li and Mg-10%Li. Furthermore, I can also identify dominant deformation mode(s) as a function of strain.

Figure 6.13(a-b) shows the relative activity, $R$, graphs for Mg-0%Li and Mg-10%Li as a function of strain. Sub-figures (a) and (b) are grouped according to solid solution hardening (basal and CTWs) or softening (pyramidal and TTW) of deformation modes with Li addition. It can be seen in this figure that Mg-10%Li NC samples show less basal or CTW activity, and more pyramidal or TTW activity. Basal slip dominates the initial stages of the plasticity in pure Mg, while pyramidal slip accommodates most of the deformation in the Mg-10%Li alloy. Thus, the easy nucleation of pyramidal dislocations as indicated by higher activity enhances the plasticity in Mg-Li alloys and also causes a solid solution softening. At high strains (> 4%), twinning occurs. With increase in strain, basal and pyramidal slip systems show rapid decrease in activity $R$. For both the compositions, TTW becomes the major deformation mode accommodating the deformation above 4% strain. The decrease in hardening rate after yielding coincides with TTW nucleation and propagation. CTW has negligible contribution above 6% strain. The addition of Li increases TTW activity and further reduces the CTW activity.

The increase in $\langle c + a \rangle$ activity with Li addition agrees with previous experimental and simulation studies of Agnew et al. [6, 31, 32] and Ando et al. [145]. Other experiments have also suggested a qualitative increase in $\langle c + a \rangle$ activity with Li addition [50, 31] but quantitative insights came only in 2001 from the combined experimental and texture simulations study of Agnew et al. [6]. Here I have successfully implemented the approach of Agnew
Figure 6.13. The contribution of each deformation mode to total deformation, the so called *relative activity*, is shown as a function of the strain and Li addition. PD refers to pyramidal type I dislocations. (a) Basal and CTW1/CTW2 modes show less activity with the Li addition, which suggests hardening for these slip systems. Inset shows the magnified view at high strains. (b) Pyramidal and TTW modes show an increased activity, suggesting softening with Li addition. These figures also show the dominant deformation mechanisms in the early stage of plasticity (basal or pyramidal) and at high plastic strains (TTW). CTWs contribution at high strains is low in Mg-0%Li and Mg-10%Li.
et al. to quantitatively show the enhancement of \( \langle c + a \rangle \) pyramidal slip due to Li addition. To my best knowledge, this is the first such attempt to atomistically calculate activity and study the effect of Li addition on slip.

6.7. Effects of different parameters such as composition, loading direction, and grain size on the strength and deformation mechanisms of NC Mg-Li alloys

In this chapter, I presented the results for representative cases of deformations for pure Mg and Mg-10\%Li. In this section, I will present the results of variation of different parameters on strength and deformation mechanisms of the NC Mg-Li alloys to generalize the conclusions. These different parameters include different Li compositions such as 5\% Li, different random distribution of Li at 10 \%Li composition, and different uniaxial loading direction and slower strain rate.

6.7.1. Different compositions of Li additions for Mg-Li alloys

In this subsection, I will present the strength and deformation results for the Mg-5\%Li composition (see figure 6.14(a-b)). As shown here, the yield point is at 0.83 GPa, which falls in between 0.77 GPa and 0.91 GPa of pure Mg and Mg-10\%Li compositions. At 5\% strain, basal dislocations, pyramidal dislocations, and TTW are also observed. Thus, the results are consistent and quantitatively interpolate between pure Mg and Mg-10\%Li composition.

6.7.2. Effect of uniaxial compression along Y direction

The uniaxial loading along different direction gives different random distribution of grain boundaries and of Li atoms in the simulation sytem. This testing will create a different simulation setup to understand the strength and deformation mechanisms in the NC Mg-Li alloys. Figure 6.15 shows the stress-strain graph for pure Mg and Mg-10\%Li alloy uniaxially loaded along the Y direction. The 23 \% decrease in yield stress labeled as \( Y \) on this figure with the addition of Li is qualitatively consistent with previously presented results for loading along the Z direction shown in figure 6.10. The deformation mechanisms for this loading are same as loading along the Z direction. Refer to figures 6.11 and 6.12 for deformation mechanisms.
6.7.3. Effect of grain size variation

In this subsection, I will present the deformations of 7nm and 20nm average grain size NC Mg-Li alloys. The variation in grain size will give more statistical data for the effect of the Li addition on deformations of NC Mg-Li alloys. Figure 6.16 and 6.17 show the stress-strain graph for 7nm and 20nm average grain sized NC Mg-Li alloys.

As seen in figure 6.16(a), the yield strength for the 7nm grain size NC decreases by 15% with 10%Li addition. This yield strength result is quantitatively consistent with the 13nm grain size NC alloys. Although, the microstructure evolution at 6% strain shown in figure 6.16(b) for pure Mg shows that the deformation is mainly accommodated by basal and pyramidal dislocations. No twins are observed until 7% strain. The absence of other deformation modes to accommodate the compression results in the highly serrated behavior in the stress-strain graph.

Figure 6.17 shows the stress-strain graph for the 20nm average grain size NC alloys. The yield strength decreases by same 15% as in 7nm and 13nm grain size cases with the 10%Li addition. This indicates good quantitative matching between different grain sizes for
Figure 6.15. Figure shows the stress-strain graph for the NC pure Mg and Mg-10%Li alloy compressed along the Y direction. The stress-strain graph shows the decrease in yield strength $Y$ from 0.98 GPa to 0.75 GPa with the addition of 10%Li in pure Mg. The decrease of 23% in yield strength with 10%Li addition is qualitatively consistent with previously presented results for uniaxial compression along the Z direction shown in figure 6.10.

NC alloys. The deformation mechanisms for this grain size is same as the 13nm grain size and is therefore not shown here.

6.8. Conclusions

I have presented a systematic study of the effect of Li addition on plasticity in NC Mg-Li alloys. Li addition is found to affect the balance of deformation modes that contribute to deformation. 10%Li addition is shown to reduce the plastic anisotropy by enhancing $\langle c+a \rangle$ pyramidal slip and TTW and reducing the basal slip and CTW activity. The hardening or softening of individual modes is explained by the relative activity of each mode in the NC samples.

Li addition decreases compressive yield strength and increases the plasticity by higher contribution of $\langle c+a \rangle$ pyramidal and TTW activity during deformation. Basal dislocations and pyramidal type I dislocations dominate the initial stages of plasticity and twins nucleate
Figure 6.16. Figure shows the results of deformation for the 7nm grain size NC pure Mg and Mg-10\%Li alloy. (a) Stress-strain graph shows that the yield strength $Y$ decreases by 15\% with the addition of 10\%Li. Yield strength for pure Mg is 0.69 GPa, whereas for Mg-10\%Li its 0.58 GPa. (b) Microstructure evolution for NC pure Mg. For this grain size, the deformation is mainly accommodated by basal and pyramidal dislocations. Twins are not observed until 7\% strain. The absence of other deformation modes create small cracks in the system and leads to highly serrated behavior in the stress-strain graph as compared to bigger 13nm grain size systems.

at higher strains. The dissociation reactions for pyramidal type I are also identified for our CDEAM potential.

To generalize the results, the effects of variation of different parameters such as Li composition, Li atoms distribution, and grain size on the strength and deformation mechanisms of NC Mg-Li alloys. These parameters show quantitatively and qualitatively consistent results for NC Mg-Li deformations.

In summary, Li addition to Mg reduces the plastic anisotropy in the hcp NC Mg-Li alloys by increasing $\langle c + a \rangle$ pyramidal and TTW activity, and reducing basal and CTW activity.
Figure 6.17. Figure shows the stress-strain graph for 20nm grain size NC pure Mg and Mg-10%Li alloy. Yield strength $Y$ decreases by 15% with the 10%Li addition. The microstructure evolution is same as in 13nm grain size system.
CHAPTER 7

SINGLE CRYSTAL SIMULATIONS OF MG-LI ALLOYS TO EXPLAIN THE OBSERVED PHENOMENA IN NANOCRYSTALLINE MG-LI SYSTEM

7.1. Introduction

In this chapter, I study the effect of Li addition on each independent deformation mode in single crystal Mg-Li system. This effect will be correlated with complex deformation modes in nanocrystalline (NC) simulations.

I use two parameters to quantify how Li addition influences the relative ease of activating each slip system in single crystal Mg. These two parameters are dislocation nucleation stress ($\tau_{NS}$) and planar stacking and twin fault energies. The quantification of deformation processes in a single crystal Mg-Li system is used to explain the effect of the Li addition on deformations in NC Mg-Li systems, and especially understand the reduction in plastic anisotropy between basal and non-basal slip systems and the increase in formability.

7.2. Nucleation stresses for each deformation mechanism

The stress to nucleate each dislocation type measures the relative ease of their nucleation, and this can be measured as a function of Li concentration. The increase in nucleation stress reflects the presence of solid solution hardening and vice-versa suggests solid solution softening.

For each type of deformation mode (basal, pyramidal-I and twins), I chose the single crystal orientation relative to the loading direction so as to maximize the Schmid factor for that slip system. To mimic the effect of grain boundaries present in the NC simulation, I introduce lenticular cracks and free surfaces in single crystal Mg and Mg-Li alloys. This promotes heterogeneous nucleation site for basal and pyramidal dislocations when systems are loaded under tension. The simulation system has a free boundary condition along the tensile direction and periodic boundaries along the two orthogonal directions. Lenticular cracks are not used in our twinning deformation simulations. For twins nucleation studies, free surfaces are used in all the directions, again to replicate the heterogeneous nucleation
sites, and grain boundary effect in NC simulations. Simulations are tensile strain controlled in that the top and bottom few layers are held fixed to apply strain. To ensure consistencies, I used the same orientations and boundary conditions for deformations to analyze the effect of the Li addition on the deformation of Mg. I do not present the results for compression deformations here as the stress required to nucleate the dislocation is $\sim$3 to 4 times higher than in tensile deformations and in NC simulations.

The supercell contains 20*60*60 unit cells along X, Y, and Z directions respectively. The orientations used for each deformation mode are shown in the figure 7.1, and tensile loading is along the Z direction. For basal and pyramidal dislocations, X and Y directions are periodic. The Z direction has non-periodic boundary conditions and is normal to lenticular crack surface. The lenticular crack is along the Y direction. For twins, all the directions are non-periodic and there is no lenticular crack. These calculations are done at 100K. Each simulation system is first annealed at 100K for 100ps using the 1fs time step to reduce the surface stress to <$5\text{MPa}$. Berendsen barostat is used to control the pressure along periodic boundaries and temperature of the atoms is maintained at 100K by explicitly rescaling the velocities of the atoms. For Mg-Li alloys, Li atoms are substituted at random positions and the structure is annealed at 100K. Averages from three random distributions of Li atoms are obtained for Mg-Li alloys simulations, and nucleation stress for each sample is within 1% of the average value. For example, the dislocation nucleation stress for basal slip system with three different random distributions of 10 at.% Li is 1.78, 1.82, and 1.85 GPa which is about 1% of the variation from the average value.

The stress-strain curves and snapshots of the dislocation nucleation for each deformation mode are shown in figure 7.1. The dislocation nucleation strains and corresponding stresses are marked as N in this figure for pure Mg and Mg-10%Li alloy. Snapshots are shown for each deformation mode at point N. At strains below point N, systems are elastic with no defects. Therefore, point N also represents the yield strength of the sample. For CTW2, full prismatic dislocations nucleate at yield point because its Schmid factor is higher than CTW2. CTW2 nucleates when stress starts to drop, and the corresponding nucleation point
Figure 7.1. The stress-strain curve and the corresponding dislocation nucleation processes are shown here. $N$ represents the dislocation nucleation points. Red, green, and blue atoms represent the hcp, (fcc) basal stacking fault, and bcc type respectively. Grey atoms are present in either disordered or in pyramidal type I dislocation core. The corresponding microstructure at point $N$ in stress-strain graph is shown for (a-b) basal dislocation (c-d) pyramidal type I dislocation. (e-f) TTW. (g-h) CTW2.
for Mg-0%Li and Mg-10%Li are shown in figure 7.1(g). I did not find any other orientation that promote nucleation of only CTW2 at yield point. I do not report single crystal results for CTW1 because I could not find any single crystal orientation to nucleate it.

Nucleation stress increases for basal and CTW1 mechanisms with increasing Li concentration, which means these deformation modes show solid solution hardening. This hardening is consistent with the diminishing activity of these deformation processes in Mg-Li NC materials. Pyramidal type-I and TTW modes show decrease in nucleation stress with the Li addition. This suggests a solid solution softening for these deformation modes and explains their increased activity in NC Mg with Li addition.

Yoshinaga et al. [5] observed similar qualitative trends experimentally for basal and pyramidal dislocations. They found solid solution hardening for basal planes and softening for pyramidal planes which confirms the present results. Agnew et al. [31] also found an increased activity of \( \langle c + a \rangle \) pyramidal dislocations and decreased activity for basal dislocations with the addition of Li in transmission electron microscopy characterization experiments, which suggest a softening of pyramidal slip system with the addition of Li. Therefore, the effect of Li addition on the nucleation of each deformation mode in single crystals helps us understand the effect of Li in NC system.

7.3. Stacking and twin fault energy

Unstable stacking fault energy (USFE) and unstable twin fault energy (UTFE) values are the barriers to nucleate the fault on a particular plane. The dissociation width and stability of the fault is given by stable fault energies (FE). So, I calculate the USFE and UTFE to check the effect of Li addition in single crystal Mg and complement the results obtained for NC simulations.

I used the methodology of Yasi et al. [123] to calculate basal SFE and Noagaret et al. [136] to calculate the pyramidal type I SFE. For TFE calculations, I use the approach of Wang et al. and Yuasa et al. [146, 147, 148]. For Mg-Li alloys, calculations are done by randomly distributing the Li atoms in the simulation cell. The SFE variation for the
Figure 7.2. SFE surfaces for (a) basal plane and (b) pyramidal dislocation type I along \(<c\>\{1\overline{1}02\rangle\) direction. (c-e) are TF energy surfaces for TTW, CTW1, and CTW2, respectively. Point (i) represents the stable SF structure for corresponding twin plane, which is used as the starting point to calculate the TFE. Point (ii) represents the stable TF structure.
different random distributions of Li is less than 2mJ/m² and so the error bars are not shown in figures.

Figure 7.2(a-b) shows the SFE as a function of the Li concentration for basal and pyramidal dislocations. For pyramidal type I dislocations, only fault F1 is observed in the NC system (see figure 6.7(a)). So, here I discuss the USFE for the pyramidal plane fault F1. The SFE surfaces for pure Mg match with those determined by Yasi et al. [123] for basal plane and with Nogaret et al. [136] for pyramidal type I. The USFE for basal plane increases by 40mJ/m² and for pyramidal type I dislocation by 20mJ/m² with 10% Li addition. This indicates a greater hardening for basal plane than pyramidal dislocations. The greater increase in basal SFE indicates that the dissociation width on this slip system decreases with addition of Li. Although the USFE for pyramidal fault increases, the increase in USFE for basal plane is about twice that of pyramidal slip system. Thus, pyramidal system accommodates a large fraction of slip than the basal slip system in Mg-Li alloys. I will also look at how the combined effect of basal and pyramidal USFE improves the formability of Mg-Li in sub-section 7.4.2.

Figure 7.2(c-e) shows the TFE surface for TTW, CTW1, and CTW2, respectively. The TFE calculation starts with a the stable stacking fault system on the corresponding plane. The layers above the stacking fault are then displaced to generate the TFE [146, 148]. Note that the combination of shear and atomic shuffle created the twins in hcp Mg and Mg-Li alloys. This mechanism of twin formation is different from fcc materials where twins form by pure shear [41]. Point (i) shown in these figures corresponds to the stable stacking fault, which is used as a reference to calculate the TFE. The UTFE is the barrier to nucleate a stable twin fault which occurs at point (ii). As seen in figures 7.2(c-e), the UTFE for TTW decreases with the Li addition and increases for both types of CTW, which is consistent with the higher TTW activity and less CTW activity in NC Mg-Li samples. Thus, the single crystal USFE and UTFE curves satisfactorily explain the effect of Li on deformation mechanisms in NC simulations.
The SFE and TFE calculations are Molecular static (MS) calculations, and are time and strain rate independent. Unlike these calculations, Molecular dynamics (MD) calculations have the time and strain rates limited by magnitude of upto maximum nanoseconds and minimum $10^7$ /second respectively. The MS calculations, being time and strain rate independent, give the barriers for a particular mechanisms and can be directly related to experiments. In this case the barriers to nucleate faults are given by USFE and UTFE. These calculations agree well with transmission electron microscopy results of Agnew et al. [31] where they observed less basal dislocations and more pyramidal dislocations with Li addition. The present study shows a higher increase in basal USFE as compared to pyramidal dislocations which implies a decrease in dissociation width of basal dislocations, which finally leads to less amount of presence of basal dislocations in Mg-Li alloys. The dissociation width of the basal dislocations decreases from 2.7nm for pure Mg to 1.9nm for Mg-10 at.%Li. Thus these MS results support the dynamic calculations done in this dissertation.

7.4. Reduction in plastic anisotropy

HCP Mg is anisotropic and has lower ductility and formability because of the large difference in nucleation stresses ($\sim 10^2$) for basal and non-basal dislocation systems at micrometer grain sizes. Its deformation is dominated by $\langle a \rangle$ basal slip. Two methods were proposed to reduce this anisotropy [6, 28]: (i) reducing the grain sizes from bulk to nanoscale activates all the deformation modes. (ii) alloying can harden or soften a deformation mode preferentially. Both the approaches reduce the nucleation stress difference between basal and non-basal slip modes (see figure 6.1).

In the present work, since I am already dealing with nm size Mg and Mg-Li grains, I will investigate the effect of the solute element (Li) addition on plastic anisotropy. Li addition has been shown to harden basal and CTW modes, and soften pyramidal and TTW modes thereby suggesting a decrease in plastic anisotropy between basal and non-basal slip systems. To explain this, I use nucleation stress for defects ($\tau_{NS}$) and unstable stacking fault energy (USFE).
7.4.1. Reduction in Plastic anisotropy: Role of dislocation nucleation stress

Figure 7.3 shows the first criterion based on \( (\tau_{NS}) \) that is expressed as,

\[
\tau_{NS} = \sigma_{nucleation} \ast m
\]

Where \( \sigma_{nucleation} \) is the nucleation stress for a particular deformation mode during tensile deformations and is taken as the point \( N \) marked in figure 7.1, and \( m \) is the Schmid factor calculated from the orientation between the loading and slip directions for a particular deformation mode. The work by Tschopp et al. [149] discuss the effect of the Schmid factor and normal factor of resolved shear stress on dislocation nucleation in fcc materials. Here we propose the plastic anisotropy criterion based on Schmid factor (see equation 64), which resolves the applied stress in the slip direction so that the nucleation stresses for different slip systems in the hcp structure can be normalized and compared in one scale as shown in figure 7.3.

![Figure 7.3](image)

**Figure 7.3.** Dislocation nucleation stress \( (\tau_{NS}) \) for each deformation mode as a function of Li concentration is presented.

Pure Mg shows the lowest value of \( \tau_{NS} \) for basal slip. This explains the dominance of the basal slip system in the pure Mg. Although the \( \tau_{NS} \) is low for CTW2, as discussed above, CTW2 nucleates after stresses are relieved by prismatic dislocations nucleation. The
prismatic dislocations have a slightly higher Schmid factor of 0.43 than CTW2 system with 0.41 in this orientation, and therefore prismatic dislocations nucleate before CTW2. So, here \( \tau_{NS} \) for CTW2 should only be taken as guidance and not as an exact value. The \( \tau_{NS} \) values for pyramidal and TTW modes are higher than for the basal slip. The observed differences between the \( \tau_{NS} \) values for basal and non-basal slip explains the origin of a factor of two in anisotropy for NC Mg.

For Mg-10\%Li, \( \tau_{NS} \) shows an increase in basal slip and CTW2, and decrease in pyramidal slip and TTW. This change in \( \tau_{NS} \) values with Li addition decreases the gap between basal and non-basal modes and reduces the plastic anisotropy. The match between basal and pyramidal \( \tau_{NS} \) values at 10\%Li composition explains the dominance of pyramidal slip at low strains in Mg-10\%Li alloys. The decrease of \( \tau_{NS} \) for TTW explains the higher activity in Mg-10\%Li at high strains. I quantify the reduction in plastic anisotropy with Li addition using a plastic anisotropy parameter \( \chi_{NS} \) defined as

\[
\chi_{NS} = \frac{\tau_{non-basal} - \tau_{basal}}{\tau_{basal}}
\]

Where, \( \tau_{NS}^{non-basal} \) is for the non-basal deformation mode in consideration and \( \tau_{NS}^{basal} \) is the for basal dislocations. These \( \tau_{NS} \) values are extracted from figure 7.3. The \( \chi \) parameter is phenomenologically similar to \( A = \tau_{CRSS}^{non-basal}/\tau_{CRSS}^{basal} \) defined by Yu et al. [28]. However, "A" parameter describes the critical resolved shear stress for dislocation motion while \( \chi \) parameter used in the present work describes the nucleation stress for different deformation modes.

This equation allows us to quantify the difficulty of nucleating deformation modes with respect to the dominant basal slip in hcp Mg. Table 7.1 shows the \( \chi \) values for pure Mg and Mg-10\%Li, and its decrease with the addition of Li. I see that the \( \chi \) value decreases by about 25\% for pyramidal 33\% for TTW with respect to the basal mode. This decrease shows the reduction of plastic anisotropy with the Li addition in the Mg-Li NC alloys.
Table 7.1. The plastic anisotropy parameter $\chi$, given by equation 65, values for pure Mg and Mg-10%Li and its decrease with the Li addition. $\tau_{NS}$ values are taken from figure 7.3.

<table>
<thead>
<tr>
<th>$\chi$ (At %Li)</th>
<th>Pyramidal</th>
<th>TTW</th>
<th>CTW</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi$ (Mg-0%Li)</td>
<td>1.32</td>
<td>2.28</td>
<td>1.1</td>
</tr>
<tr>
<td>$\chi$ (Mg-10%Li)</td>
<td>1</td>
<td>1.53</td>
<td>1.1</td>
</tr>
<tr>
<td>% decrease in $\chi$</td>
<td>24.24</td>
<td>32.89</td>
<td>0</td>
</tr>
</tbody>
</table>

7.4.2. Reduction in Plastic anisotropy: Role of stacking and twin fault energy

Equation 66 shown below is for the second criterion based on the unstable stacking fault energy. Moitra et al. [65] defined a formability parameter in equation 66 as the ratio of unstable stacking fault energies.

$$
\chi_{usf} = \frac{(\gamma_{B_{usf}})^X}{(\gamma_{P_{usf}})^Mg} \frac{X}{(\gamma_{B_{usf}})^Mg} \frac{X}{(\gamma_{P_{usf}})^Mg}
$$

Here, $\gamma_{usf}$ is an unstable stacking fault energy, $B$ and $P$ refer to basal and pyramidal stacking faults respectively, and $X$ is the Mg-10%Li alloy concentration.

This parameter is calibrated by Moitra et al. for different solute additions in Mg. They found that, if $\chi_{usf} > 1$, the alloying addition increases the formability. It accounts for the ratio of pyramidal to basal unstable stacking fault energies in Mg-Li alloys and pure Mg. The present CDEAM potential gives value of 1.3 for Mg-10%Li alloy and therefore, increases formability.

However, Moitra et al. did not explain how the ratio of unstable stacking fault energies is connected to the formability of the materials. In this work, we propose a new formability
parameter derived from physical considerations of lattice friction for dislocation motion. Note that the present work is mainly based on the nucleation of dislocations, and here we show the preliminary results of lattice friction. Detailed analysis required to implement a criterion based on motion of dislocations is beyond the scope of this work.

As a first approximation, we consider the lattice friction given by a simple Peierls-Nabarro model in which dislocations remain planar and the generalized stacking fault energy can be described by a sinusoidal function. Under these assumptions, the lattice friction is proportional to the exponential of \((-Kb/\gamma_{usf})\). Here \(K\) is the shear modulus, \(b\) is the magnitude of the Burgers vector, and \(\gamma_{usf}\) is the unstable stacking fault energy respectively. Here the addition of Li changes the lattice friction of Mg. When written in terms of lattice friction, the formability parameter is proportional to the difference of the inverse of the unstable stacking fault energies. Therefore, I define the formability parameter \((F_p)\) as equation 67.

\[
(67) \qquad F_p = K_{(c+a)}b_{(c+a)} \left[ \frac{1}{(\gamma_{usf}^P)_{Mg}} - \frac{1}{(\gamma_{usf}^P)_{X}} \right] - K_{(a)}b_{(a)} \left[ \frac{1}{(\gamma_{usf}^B)_{Mg}} - \frac{1}{(\gamma_{usf}^B)_{X}} \right]
\]

Where, \(B\) and \(P\) are basal and pyramidal slips respectively, \(\gamma_{usf}\) is the USFE, \(K\) is the shear modulus, and \(b\) is the Burgers vector.

The \(F_p\) value defined above is 9.2, which is greater than 1. As per Moitra et al. [65] calibration for the previous \(\chi_{usf}\) parameter, a value greater than 1 suggests increase in formability. To evaluate this criteria we used the \(\gamma_{usf}\) data from Moitra et al. for Mg-Li and Mg-Al, and calculate \(F_p\) value. For these alloy systems, we used the variation of \(K\) and \(b\) for Mg-Li system from the CD-EAM Mg-Li potential and for Mg-Al system from Liu et al. potential [150] as these values were not available in Moitra et al. work. With these inputs, the \(F_p\) value comes out to be 17.4, and 11.3 for the two alloy systems respectively. All these values are greater than 1. Thus we can argue that CD-EAM Mg-Li potential predicts the correct qualitative trend for increase in formability.
7.5. Conclusions

In this chapter, I presented the effect of Li addition in single crystal Mg and correlated it to nanocrystalline Mg-Li results. Nucleation stress ($\tau_{NS}$) and unstable fault energy (UFE) are evaluated for each deformation mode to explain the observed phenomena in nanocrystalline simulations from previous chapters. There is inverse relationship between the activities of different slip systems and these two parameters ($\tau_{NS}$, UFE) with Li alloying additions. This relation is qualitatively shown by the equation in figure 7.4. An increase in these parameters suggest a decrease in the activity and decrease in them suggests an increase in the activity of slip systems with the Li addition. The table in figure 7.4 shows this correspondence between nanocrystalline (NC) simulations and single crystal simulations and helps to satisfactorily explain the observed phenomena in NC simulations in previous chapter.

Stacking fault energy shows a larger increase for basal dislocations and a smaller increase for pyramidal type-I dislocations with Li addition. TTW fault energy decreases whereas the CTW1 and CTW2 fault energies increase with the Li addition. Nucleation stress increases for the basal slip and CTW mechanisms, and decreases for pyramidal slip and TTW mechanism. These two factors, fault energies and nucleation stress, explain the lower basal/CTW and larger pyramidal/TTW activities in Mg-Li NC samples.

Furthermore, fault energy calculations and the reduction in plastic anisotropy are time independent MS calculations. They will accurately describe the barrier to nucleate dislocations on a given slip system. The results from these MS simulations are also consistent with the MD simulations in the previous chapter.

In summary, the Li addition to Mg increased the formability by reducing the plastic anisotropy in the hcp NC Mg-Li alloys. This is caused by the enhanced $\langle c + a \rangle$ pyramidal slip and TTW activity and reduced basal slip and CTW activity.
Figure 7.4. Figure summarizes the results in this chapter. The equation shows the inverse relationship between slip system activities in nanocrystalline (NC) simulations and nucleation stress ($\tau_{NS}$) or unstable fault energies (UFE). The table shows the effect of addition of Li in NC simulations on activity of different slip systems. The $\tau_{NS}$ and UFE’s show the corresponding increase or decrease in the values for the respective slip systems. Therefore, $\tau_{NS}$ and UFE in single crystal simulations satisfactorily explain the effect of Li addition in NC simulations.
CHAPTER 8

CONCLUSIONS AND FUTURE STUDIES

8.1. Conclusions

The dissertation consists of two parts. In the first part, I created a reliable and transferable concentration dependent interatomic potential for hcp and bcc phase Mg-Li alloys. This model is based on first principles and experimental data, and it reproduces different fundamental physical properties for Mg-Li alloys reasonably well. In addition, the Mg-Li phase diagram and stacking fault energy (SFE) predictions are in excellent agreement with previous experimental assessments. The CD-EAM formalism proposes a viable solution for capturing the thermodynamics of two separate phases in the Mg-Li binary alloy system. These predictions indicate the reliability of our potential. Thus, this potential can be reliably used to study the deformation mechanisms in these alloys due to precipitate-dislocation interactions, effect of alloying additions on defect energetics, and effect of precipitation at the interfaces.

In the second part, I study the effect of Li addition on the plasticity in NC Mg using the computer simulations. These studies indicate that the Li addition affects the activities of slip systems that contribute to deformation. 10%Li addition reduces the plastic anisotropy by enhancing \((c + a)\) pyramidal slip and TTW activity, and reduces the basal slip and CTW activity. The solid solution hardening or softening is explained using the relative activity of each mode in NC using values of fault energies and nucleation stress \((\tau_{NS})\) in single crystals. Li addition decreases compressive yield strength and increases the plasticity by enhancing the contribution of \((c + a)\) pyramidal and TTW activities. Basal and pyramidal type-I dislocations dominate the initial stages of plasticity while twins nucleate at higher strains. The dissociation reactions for pyramidal type-I are also identified for our CD-EAM potential. To generalize the results, the effects of variation of Li composition, Li distribution, and grain size on the strength and deformation mechanisms of NC Mg-Li alloys.
were investigated. These parameters show quantitative and qualitatively consistent results for NC Mg-Li deformations.

In single crystals, stacking fault energy increases at a faster rate for basal dislocations than for pyramidal type-I dislocations with Li addition. TTW fault energy decreases whereas basal slip, CTW1 and CTW2 fault energies increase with Li addition. Dislocation nucleation stress increases for basal and CTW systems and decreases for pyramidal and TTW systems. This suggests a solid solution hardening for basal plane, CTW1 and CTW2, and relative solid solution softening for pyramidal type-I and twinning systems. The fault energy calculations are significant since these are molecular statics simulations, that are independent of time and strain rate effects. Unlike the nanocrystalline deformation simulations which are dynamic and have these limitations, the fault energy calculations add another dimension to the results. They accurately describe the energy barrier, and the results from these simulations match well with the MD simulations done in nanocrystalline Mg-Li alloys.

In summary, the Li addition to Mg increased the formability by reducing the plastic anisotropy in the hcp NC Mg-Li alloys. This is caused by the increased \( c + a \) pyramidal slip and TTW activity and reduced basal slip and CTW activity.

8.2. Future work

The present work can be extended to understand the effect of Li addition on deformation processes such as dislocation-grain boundary and dislocation-twin boundary interactions, crack nucleation and propagation during fatigue, dislocation-precipitate interaction. Strength and deformation mechanisms in special grain boundaries such as sigma boundaries or twin boundaries can also be studied. Dislocation motion parameters such as Peirls stress and dislocation velocities can be calculated and used to understand their effect in nanocrystalline deformations. Although the main focus of the present work was studying the deformation mechanisms in the hcp Mg-Li alloys, the Mg-Li interatomic potential should be reliable to study the bcc phase of this alloys as well. The bcc phase properties reliably studied in the present work are variation of heat of mixing, lattice parameter, and bulk
modulus. The phase diagram also shows the correct phase boundaries for the bcc phase. So, deformation mechanisms in the bcc should be addressed well with this potential.

The present Mg-Li CD-EAM potential limitations include appreciable deviation of properties like the higher bulk modulus for bcc phase, lower hcp to bcc transformation energy, and absence of pyramidal type II stacking fault as compared to literature data as discussed in chapter 5. Most of these properties arise from limitations of the pure Mg potential [11] used by us. If better agreement of these properties with literature is needed for different studies, the same construction method used for Mg-Li CD-EAM potential should be used with a better Mg potential. There are two other Mg potentials available in the literature by Liu et al. [121] and Pei et al. [151]. Reader can refer to these papers for description of their advantages and disadvantages.

The molecular dynamics simulations studies of the effect of Li addition in Mg-Li nanocrystalline and single crystalline in this thesis show the increase or decrease of relative activity, fault energies and nucleation stress. To understand how the Li addition affects energetics, which results in increase or decrease of a particular property, first principles calculations based on density functional theory (DFT) can be done. DFT can give the distribution of charge density that can then be used to interpret the variation in property and bonding with the Li addition. Therefore, next step in this work I propose the first principles calculations to understand how the Li addition affects the local charge distribution and bonding.
LIST OF PAPERS

The list of papers from my work during PhD.


2. **S. V. Karewar**, N. Gupta, E. Martinez, S. Groh, A. Caro, S. G. Srinivasan, Atomistic simulations of deformation mechanisms in Mg-Li alloys: From single crystals to nanocrystalline material, (Under review)


4. **S. V. Karewar**, A. Srivastava, N. Gupta, A. Needleman and S. G. Srinivasan, Effect of geometry and orientation on deformation behavior and strength of face centered cubic nanoparticles (Under preparation)

5. N. Gupta, **S. V. Karewar**, E. Martinez, S. G. Srinivasan, A. Caro, Helium trapping at nanoscale precipitate interface in metals, (Under preparation)


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[34] M. Lentz, R. Coelho, B. Camin, C. Fahrenson, N. Schaefer, S. Selve, T. Link, I. Beyelerlein, and W. Reimers, “In-situ, ex-situ EBSD and HR-TEM analyses of primary, secondary and tertiary twin development in an Mg 4 wt percent Li alloy,” *Materials Science and Engineering: A*, vol. 610, no. 0, pp. 54 – 64, 2014. 1, 17, 94


[98] H. C. Andersen, “Molecular dynamics simulations at constant pressure and/or temperature,” *The Journal of Chemical Physics*, vol. 72, no. 4, 1980. 30, 32


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